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U. S. DEPARTMENT OF AGRICULTURE.

BUREAU OF CHEMISTRY—BULLETIN No. 152.

R. E. DOOLITTLE, Acting Chief of Bureau.

PROCEEDINGS

OF THE

TWENTY-EIGHTH ANNUAL CONVENTION

OF THE

ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS,

HELD AT

WASHINGTON, D. C., NOVEMBER 20-22, 1911.

EDITED BY

HARVEY W. WILEY,
SECRETARY OF THE ASSOCIATION,

WITH THE COLLABORATION OF

A. L. PIERCE,
Editor, Bureau of Chemistry.



WASHINGTON:
GOVERNMENT PRINTING OFFICE.
1912.

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1912.

LETTER OF TRANSMITTAL.

U. S. DEPARTMENT OF AGRICULTURE,
BUREAU OF CHEMISTRY,
Washington, D. C., February 5, 1912.

SIR: I have the honor to submit for your approval the Proceedings of the Twenty-eighth Annual Convention of the Association of Official Agricultural Chemists. Owing to the steadily increasing volume of the work covered by these investigations and the importance of the detailed studies of the methods of analysis, which now are generally recognized as official in inspection work, only the reports and correlated papers, together with the specific action on the part of the association affecting the conduct of the work, are presented, all discussion being omitted. I recommend that this report be published as Bulletin No. 152 of the Bureau of Chemistry.

Respectfully,

H. W. WILEY,
Chief of Bureau.

Hon. JAMES WILSON,
Secretary of Agriculture.

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PROCEEDINGS OF TWENTY-EIGHTH ANNUAL CONVENTION OF ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

FIRST DAY.

MONDAY—MORNING SESSION.

The twenty-eighth annual convention of the Association of Official Agricultural Chemists was called to order by the president, Mr. F. W. Woll, of Madison, Wis., on the morning of November 20, at the Raleigh Hotel, Washington, D. C. The following members and visitors, 225 in number, registered:

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Adams, A. C., College Park, Md.

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REPORT ON PHOSPHORIC ACID.

By H. D. HASKINS, *Referee*, and A. J. PATTEN, *Associate Referee*.

REVIEW OF WORK DONE ON BASIC SLAG.

The work of the referee has consisted of a study of the Wagner method and its various modifications to determine if the method was applicable to the analysis of basic slags, particularly with reference to the determination of available phosphoric acid. This work seemed to be in line with the recommendations of committee A for the year 1909, "That the Wagner method for the estimation of the availability of phosphoric acid in slags be brought up for provisional adoption at the next meeting." No report on phosphoric acid was made for the season 1910 and action by the association as to the adoption of this method was deferred another year.

As considerable work on basic slag has been done from time to time by members of the association, it may not be out of place here to give a brief abstract of such work extending over a period of 15 years. In the proceedings for 1896 H. A. Huston presented a paper on the action of ammonium citrate and citric acid on basic slag. It consisted of a study of the influence of time on digestion, influence of temperature, influence of acid and alkali, influence of quantity of slag used. A comparison was also made of the Wagner method (acidulated citrate of ammonia) with the official method. A paper was also presented by H. W. Wiley on the mechanical analysis of basic slag.

In 1897 a comparison was made by H. B. McDonnell of the availability of phosphoric acid in basic slag by Wagner's method, ammonium citrate, and a 1 per cent citric acid solution. In the Proceedings for that year, upon recommendation of the committee, a description of the Wagner method was published (see pp. 72 and 73).

In 1898 H. J. Wheeler reported that at a meeting of representatives of German experiment stations which he had attended it was proposed by Wagner that a 2 per cent citric acid solution be adopted in place of the acid citrate solution previously employed, the conditions of treatment remaining the same. Wagner's suggestion was strongly supported by Maercker, of Halle, and others. The reason for the proposed change was the fact that it was difficult to secure comparative results, even on the same samples, in the various German laboratories.

At the association meeting in 1900 Mr. Macfarlane, of Canada, brought out the fact that much slag was being sold in both Canada and the United States, and emphasized the fact that the association had no adequate method of determining the available phosphoric acid in this material. He gave some analytical data and urged the adoption of some method. This was favored by Myers and some others but met with opposition. It was at this meeting that the suggestion was made concerning the commercial valuation of slags by mechanical analysis and total phosphoric acid.

In 1901 H. K. Miller included a sample of basic slag in the samples sent out for cooperative work, with instructions to analyze by a 1 per cent citric acid solution. No recommendations were made, however, concerning the analysis of slags.

In 1902 C. H. Jones as referee studied slags by the official method, the 1 per cent citric acid solution, 2 per cent citric acid solution, ammonium citrate solution diluted with an equal volume of water, and the Macfarlane method. The latter provided for the removal of the free lime in the slag by boiling with a

5 per cent ammonium chlorid solution and treating the residue with 100 cc of a 1 per cent citric acid solution, shaking every five minutes for one-half hour and determining the phosphoric acid in the washed residue. No recommendations were made, but it was suggested that work on basic slags be discontinued on account of the limited use of slags in this country.

In 1903 Hilgard took exception to the statement made in the Proceedings of the previous year "that very limited quantities of slag were used in this country" and stated that over 1,500 tons of it were used in California alone the previous year. He urged that, as the slag was guaranteed by the Wagner method, some suitable method should be provided for its analysis. A resolution was therefore adopted that the referee on phosphoric acid be instructed to reconsider the question of the valuation of basic slag, especially the recommendation to establish a standard based on the total phosphoric acid and degree of fineness.

No work was done in 1904, but the following year Mr. Williams as referee planned work on three samples of slag by four separate methods: The ammonium chlorid citric acid method, the cane sugar citric acid method, the citric acid method, and the neutral citrate of ammonia method. The recommendations were that the referee next year plan field and pot experiments with cultivated plants to study the relative value of phosphoric acid in foreign and domestic slags, redonda, and precipitated phosphates; also that further study be made on determining the total and available phosphoric acid in basic slags.

In 1905 no work was done on slags. George D. Leavens urged the adoption of some suitable method of determining available phosphoric acid in slags. It was recommended by committee A that the next referee of phosphoric acid take up methods applicable under American conditions for the examination of basic slags.

In 1907 Kilgore recommended that the fineness of the material be determined according to the plan followed with bone meal, and the commercial value estimated on the basis of total phosphoric acid and fineness of product. This recommendation, which was approved by committee A, was adopted provisionally, pending further work. The following recommendation was also made by committee A and was adopted, namely, that the referee further study the subject of basic slag with a view to devising some method for the determination of the available phosphoric acid which it contains.

In 1908 H. D. Haskins, in a paper on the mechanical analysis of slags, showed the importance of specifying the sieve mesh to be used in mechanical analysis of slags and also showed the inconsistency of the mechanical method of valuing, provided the slag was adulterated with floats or other finely ground mineral phosphate.

In 1909 no work was done, but committee A recommended:

First. That a special committee be appointed to confer with the various experiment stations to secure cooperation in cultural experiments to determine the available phosphoric acid in basic slag; also to make an annual report to the association and at the end of five years to make appropriate recommendations concerning laboratory methods.

Second. That the Wagner method be brought up for provisional adoption at the next meeting.

No work was done and no recommendations were made at our last meeting.

Acting upon the recommendation contained in the last referee's report on phosphoric acid, which was sustained by committee A, the plan of your referee has been to make a systematic study of the Wagner method with its various

modifications and in this work to enlist the cooperation of as many analysts as possible. In response to the circular letter sent out by the secretary, 10 different chemists volunteered to cooperate in the work. Eleven other men promised cooperation, in response to personal letters sent out by the referee.

Two samples were prepared and sent with the instructions during the month of March. No. 1 was a basic slag phosphate imported from Germany. No. 2 was composed of equal weights of basic slag phosphate and ground Florida rock phosphate, the two being intimately mixed. The instructions for the work were as follows:

INSTRUCTIONS FOR COOPERATIVE WORK OF 1911 ON AVAILABLE PHOSPHORIC ACID IN BASIC SLAG PHOSPHATE.

DEAR SIR: There are being sent to you by express two samples marked 1 and 2. Please have them analyzed as per methods outlined below.

1. Determine moisture at 100° C.
2. Determine total phosphoric acid on each, according to official method, using the a_7 method of making solution. (See Bul. No. 107, Revised, Bureau of Chemistry.)
3. Determine total phosphoric acid by adding to 50 cc of the filtrate 50 cc of citrate of ammonia mixture. (See solution 5.) If the solution is still acid, make neutral with ammonium hydroxid and add 25 cc of magnesia mixture. (See solution 4.) Stir 30 minutes, allow to stand two hours, filter through a platinum Gooch crucible, wash six times with 2 per cent ammonium hydroxid, and proceed as usual.
4. Determine available phosphoric acid by 2 per cent citric acid (Wagner's method), as follows:

(A) *Making the citric solution.*—Weigh 5 grams of the basic slag, transfer to a one-half liter flask containing 5 cc of 95 per cent alcohol, and make up to the mark with dilute citric acid solution (2 per cent) of a temperature of 17.5° C. Fit the flask with a rubber stopper, and put at once into the rotary apparatus for 30 minutes, making 30 to 40 revolutions per minute. Take off and filter immediately.

(B) *Analysis of the citric solution.*—As soon as the filtration is completed, analyze the solution at once according to the three following methods:

(a) *Molybdate method.*—Take 50 cc of the clear filtrate and add to it 100 cc of molybdate solution. (See solution 3.) Put the beaker into a water bath until the temperature reaches 65° C.; take out and allow to cool at ordinary temperature. Then filter, and wash the yellow precipitate of phosphomolybdate of ammonia with 1 per cent nitric acid. Now dissolve in 100 cc of 2 per cent ammonium hydroxid (cold) and add to the solution 15 cc of magnesia mixture (see solution 4), drop by drop during continuous stirring; then cover the beaker with a glass cover and allow to stand for about 2 hours. Then filter the double phosphate of ammonia and magnesia through a tared platinum Gooch crucible, wash 6 times with 2 per cent ammonium hydrate, dry, and proceed as customary for phosphoric acid determination.

(b) *Citrate of ammonia-magnesia mixture method.*—Put 100 cc of the clear filtrate into a 200 cc flask and add 50 cc of citrate magnesia mixture. (See solution 6.) Heat the flask slightly (about 15 minutes) by means of a Bunsen burner until the silicic acid has been precipitated. Shake the flask in order to conglomerate the precipitate, and continue heating to boiling point. Allow to cool, add 25 cc of hydrochloric acid of 1.124 specific gravity, and allow it to stand for about thirty minutes, during which time shake occasionally. Fill up to the mark with water, fit the flask with a rubber stopper, and shake vigorously several times till the precipitate of silicic acid has been divided into very fine particles. Then filter and add to 100 cc of the filtrate (0.5 gram basic slag) 50 cc of ammonium hydroxid (10 per cent) while stirring the contents of the beaker. Continue stirring, preferably by means of a stirring apparatus, for thirty minutes, filter the precipitate, and treat as usual.

(c) *Iron citrate of ammonia-magnesia mixture method.*—To 50 cc of the clear filtrate add at once 50 cc of iron citrate of ammonia-magnesia mixture. (See solution 7.) Cool rapidly to room temperature, stir for thirty min-

utes in a stirring apparatus, allow to stand for two hours, filter through tared platinum Gooch crucible, wash six times with 2 per cent ammonium hydroxid, and treat as usual.

PREPARATION OF SOLUTIONS.

1. *Concentrated solution of citric acid (10 per cent).*—Dissolve in water exactly 200 grams of chemically pure crystallized citric acid having its full percentage of water of crystallization. Make up this solution exactly to 2 liters. (Where a large number of analyses are to be made, 0.5 gram of salicylic acid should be added to the liter of this solution so as to preserve it.)

2. *Dilute solution of citric acid (2 per cent).*—Mix exactly 1 volume of concentrated solution of citric acid (solution No. 1) with four volumes of water. The resulting solution should have a temperature of about 17.5° C. when used.

3. *Molybdate solution.*—Put 125 grams of molybdic acid into a 1-liter flask with about 100 cc of water and dissolve by adding, while shaking, about 300 cc of 8 per cent ammonium hydroxid. Mix this solution with 400 grams of nitrate of ammonia, fill up to the mark with water, and add the whole to 1 liter of nitric acid of 1.19 specific gravity. Allow to stand for 24 hours at a temperature of 35° C. and then filter.

4. *Magnesia mixture.*—Dissolve 110 grams of pure crystallized muriate of magnesia and 140 grams of muriate of ammonia in 1,300 cc of water, and mix this solution with 700 cc of liquor of ammonia containing 8 per cent of ammonium hydroxid. Allow this mixture to stand for several days and then filter.

5. *Citrate of ammonia.*—Dissolve 100 grams citric acid in 350 cc of 24 per cent ammonium hydroxid and make to volume of 1 liter.

6. *Citrate of ammonia-magnesia mixture.*—Place 200 grams of citric acid and 40 grams of muriate of ammonia in a 1-liter flask, and add 200 cc of water, and then 500 cc of liquor of ammonia (20 per cent). Keep the flask stoppered until the contents are dissolved and cooled down. Then add 55 grams of muriate of magnesia, and fill up to the mark with water.

7. *Iron citrate of ammonia-magnesia mixture.*—To 1,000 cc of citrate of ammonia-magnesia mixture add 10 cc of the 20 per cent ferrous chlorid solution.

8. *Ferrous chlorid solution.*—Dissolve 20 grams of ferrous chlorid in 100 cc of distilled water.

FURTHER INFORMATION AND PRECAUTIONS TO BE TAKEN.

1. A photograph and detailed drawings of an inexpensive but efficient shaking apparatus accompanies the instructions for phosphoric acid work (see fig. 1). This apparatus has been in use for a number of years in the laboratory of the Massachusetts agricultural experiment station; it can be easily made by your local carpenter, and should not cost over \$8 or \$9; it also answers every purpose and obviates the necessity of purchasing an expensive apparatus listed in various catalogues at from \$27 to \$35.

2. It will sometimes be seen, when pouring the 500 cc of the citric-acid solution onto the 5 grams of basic slag, that the latter clogs somewhat, and becomes permeated only after a considerable time. In order to guard against this, 5 cc of alcohol are poured into the half-liter flask before the basic slag is put in; this insures immediate and complete permeation.

3. The rotary apparatus prescribed for shaking the flasks must not be substituted by ordinary shaking or rocker apparatus, as the latter differs in construction and effect.

4. The half-liter flasks (after the design of Wagner) must have a neck width of at least 20 mm and are marked at least 8 cm below the mouth. These two points are important; for if the neck width is too narrow and the mark too high, the result will be too low, owing to the movement of the liquid being so limited.

5. The rotary apparatus must turn round its axle 30 to 40 times per minute. Variation within these limits has no marked influence on the results.

6. The filtration must be done immediately after 30 minutes' rotation, and it is recommended to use a folded filter paper of such size that the whole quantity of liquid can be poured onto the filter at once. Small and bad filtering papers give rise to error, in consequence of too slow filtration. If at first the

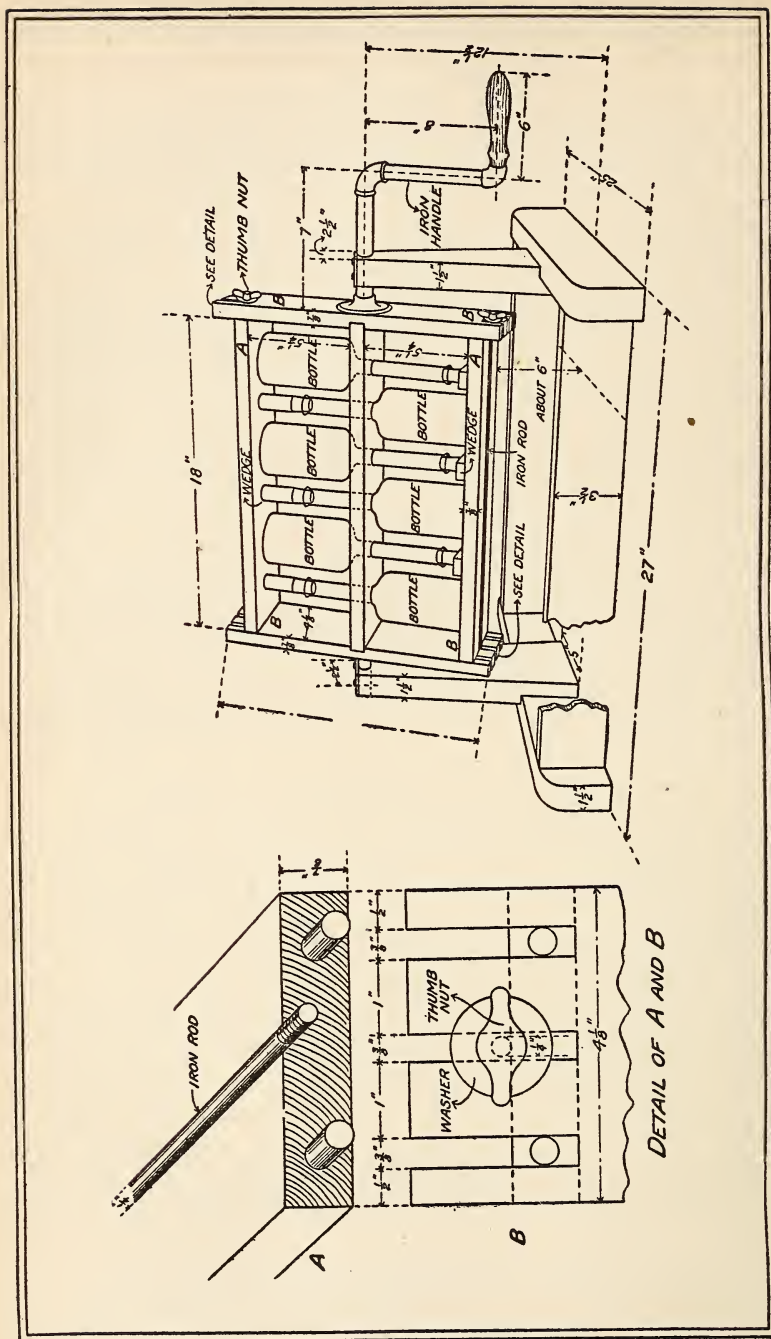


FIG. 1.—Agitating apparatus for phosphoric acid determination.

filtrate is not clear, it must be again filtered (through the same filter) until it becomes clear.

7. After filtering the citric solution of the basic slag, the precipitation of the phosphoric acid should be carried along without delay, as long standing increases the tendency of the silica to precipitate during the operation.

8. If the beaker containing the mixture of phosphatic and molybdic solutions is put into the water bath until the temperature reaches between 60° and 70° C, a precipitate free from silicic acid results. If heating is continued for a considerably longer time, the precipitate will often be mixed with silicic acid, especially when the molybdic solution is not added to the filtrate immediately, but only after 6 to 12 hours (or longer) after filtration. If silicic acid is present, the precipitate dissolves slowly in ammonium hydroxid, but at first not clearly. Special attention must be paid to the point that the yellow precipitate is dissolved quickly and quite clearly by ammonium hydroxid (2 per cent) not made warm. If the solution becomes clear only after some time, molybdic solution and nitric acid must be added to same in order to get a pure precipitate of phospho-molybdate of ammonia; in other words, the phosphoric acid must be reprecipitated by the molybdic solution.

Please return results to the referee as early as possible. The samples have been sent out early so that the work may be taken up before the rush of the fertilizer inspection begins in the various States. It is to be hoped that results may reach the referee by the first of August at the latest. An earlier report than this will be appreciated.

Very truly yours,

H. D. HASKINS,
Referee on Phosphoric Acid.

TABULATED RESULTS OF COLLABORATIVE WORK.

TABLE 1.—Comparative work on basic slag.

COMPARATIVE RESULTS.

Chemist.	Moist- ure.		Total phosphoric acid.				Available phosphoric acid.					
			Sample 1.		Sample 2.		Sample 1.			Sample 2.		
	No. 1.	No. 2.	Official method.		Special method.		Molybdic method (a).	Citrate of ammonia-magnesia mixture method (b).	Iron citrate of ammonia-magnesia mixture method (c).	Molybdic method (a).	Citrate of ammonia-magnesia mixture method (b).	Iron citrate of ammonia-magnesia mixture method (c).
A. J. Patten, Michigan.....	0.19	0.39	17.57	24.42	15.17	15.43	15.42	8.59	8.69	8.50
Wm. C. Marti, Michigan.....			17.92	17.57	24.70	24.47	15.28	15.20	15.32	8.73	8.37	8.53
C. van Cornell, South Carolina.....	.29	.45	17.54	17.15	24.50	24.84	15.36	15.75	17.40	19.46	8.44	8.94
A. W. Clark, New York.....	.14	.21	17.98	17.88	24.67	24.58	14.78	14.62	14.54	8.32	8.00	7.45
E. G. Proulx, Indiana.....	.19	.26	17.85	18.41	24.75	24.81	15.10	15.31	17.52	9.08	9.10	8.64
P. L. McCreary and P. L. Hibbard, California.....	.21	.45	18.88	122.84	25.20	25.01	15.16	15.44	15.45	29.17	8.78	8.76
L. S. Walker, Massachusetts.....	.23	.92	18.60	18.22	25.17	24.84	14.51	14.81	14.46	8.25	9.08	8.09
E. S. Erb, Pennsylvania.....			17.75	24.34	14.95	8.53
W. L. Whitehouse, Pennsylvania.....	.15	.22	17.69	17.85	24.44	24.98	14.93	8.38
L. T. Bowser, Ohio.....	.13	.29	18.22	18.15	24.98	24.68	15.28	15.27	17.46	8.51	8.96	8.24
Average.....	.19	.40	18.11	17.89	24.78	24.80	15.05	15.25	15.89	8.55	8.68	8.42

¹ Not included in average.

² Precipitate of magnesium pyrophosphate allowed to stand overnight, No. 2 not included in average.

TABLE 1.—Comparative work on basic slag—Continued.

ADDITIONAL DATA USING MODIFIED METHODS.

Modified methods used in basic slag analysis.	Sample No.	California Experiment Station.	W. L. Whitehouse, Coe-Mortimer Co.	L. T. Bowser, Dayton, Ohio.
Total phosphoric acid:				
Official α_7 , volumetric method.....	1	17.93
Official gravimetric method after separation of silica by dehydration.....	2	24.37
Official volumetric method after separation of silica by dehydration.....	1	17.85
Official volumetric method after separation of silica by dehydration.....	2	24.65
Official volumetric method after separation of silica by dehydration.....	1	17.80
Official volumetric method after separation of silica by dehydration.....	2	24.55
Available phosphoric acid:				
Molybdate method, except ammonia solution was neutralized with hydrochloric acid before adding magnesia mixture. Strong ammonium hydroxid added after 15 minutes.....	1	15.16
Molybdate method, except that yellow precipitate was titrated as per volumetric method.....	2	8.80
Molybdate method, except that yellow precipitate was titrated as per volumetric method.....	1	15.00
Molybdate method, except that yellow precipitate was titrated as per volumetric method.....	2	8.50
Yellow precipitate was obtained by official volumetric method and determinations made volumetrically.....	1	15.00
Yellow precipitate was obtained by official volumetric method and determinations made volumetrically.....	2	8.65
Wagner gravimetric method, except that molybdic solution and magnesia mixture were made according to the official methods.....	1	14.95
Wagner gravimetric method, except that molybdic solution and magnesia mixture were made according to the official methods.....	2	8.37
Procedure as under "3" for total phosphoric acid, i. e., without separation of silica.....	1	15.06
Procedure as under "3" for total phosphoric acid, i. e., without separation of silica.....	2	8.68

COMMENTS BY ANALYSTS.

E. G. Proulx, La Fayette, Ind.: In the estimation of total and available phosphoric acid several solutions were made up and determinations were made from the same solution, using different methods.

In the case of sample No. 2 the results obtained by the citrate of ammonia mixture method for total phosphoric acid agree well with those obtained by the official method, but the former apparently is not applicable with No. 1, as the final precipitate was contaminated with iron. The magnesia ammonium phosphate also precipitates slowly, requiring constant stirring for at least 20 minutes.

The molybdic method for the determination of available phosphoric acid gave concordant results. One objection to this method, however, lies in the use of 100 cc of 2 per cent ammonium hydroxid in dissolving the ammonium phosphomolybdate, as there is some danger of magnesia precipitating in a solution containing this quantity of ammonia.

The results obtained by the molybdate method and the citrate of ammonia magnesia method agree very well, although in using the latter method it required constant stirring for one hour to bring down the magnesia-ammonium phosphate.

The results obtained with the iron-citrate of ammonia-magnesia mixture method were of uncertain value. With sample No. 1 the final precipitate was contaminated with iron, which accounts for the high percentage of available phosphoric acid. Using this method it was necessary to employ ashless filter paper in order to filter off the magnesia-ammonium phosphate, as the solution would not pass through a platinum Gooch crucible. In order to obtain a pure precipitate of magnesia-ammonium phosphate the phosphoric acid in four separate aliquots from different solutions was precipitated and the double phosphate of magnesia and ammonium purified by dissolving in dilute hydrochloric acid and again precipitating by the addition of ammonium hydroxid and a few drops of magnesia mixture. This procedure resulted in final precipitates free from iron, and the results obtained agreed well with those secured by the molybdate method. In one other instance the magnesia-ammonium phosphate was purified by dissolving in dilute hydrochloric acid, neutralizing with ammonia, then acidifying with nitric acid, and completing the work according to the official method. This gave a white precipitate with result concordant with those obtained by the molybdate method. The molybdate and the citrate of ammonium-magnesia mixture methods are easy of manipulation and apparently gave correct results, while, on the other hand, the iron-citrate of ammonia-magnesia mixture method gave results of uncertain value and the method must be modified in order to be of value in the determination of available phosphoric acid in basic slag phosphates.

P. L. McCreary and P. L. Hibbard, California: In the opinion of the analysts, Messrs. P. L. McCreary and P. L. Hibbard, who did all of the work reported on, the volumetric method is much more satisfactory on basic slag than is the gravimetric method, particularly where there are quantities of soluble silica present. This is indicated in connection with subdivision 2, determination of total phosphoric acid. On comparison of the results under this subdivision you will note the close agreement between the volumetric determinations and the gravimetric determination made after dehydration and separation of silica, and also the difference between the results so obtained by the gravimetric method without the separation of silica. With regard to subdivision 3, determination of total phosphoric acid by the citrate of ammonia-magnesia mixture method, you will note the very wide discrepancy in the case of sample No. 1 between the figures obtained by this method and those obtained by method No. 2 in all its modifications. It would seem that this last method is totally inapplicable in the presence of large quantities of soluble silica. In our opinion the directions should be modified somewhat; the ammonia should be neutralized before the addition of the magnesium mixture.

W. L. Whitehouse, Coe-Mortimer Co.: In addition to the other work, I have made determinations by the Wagner method, modifying same by using the official molybdate and magnesia solutions in place of those prescribed by Wagner.

My motive in making the latter determinations was to ascertain whether or not these official solutions could be substituted for the Wagner solutions without seriously affecting the method. If this substitution did not seriously affect the method there would be eliminated the necessity of carrying the two solutions in stock. The results of this substitution you will note are highly gratifying.

L. T. Bowser, Dayton, Ohio: My results on No. 2 by the official method were not entirely satisfactory, but I could spare no more time to repeat the determination. Methods 2 and 3 check very well, it appears. With the available phosphoric acid the making of the solution went very satisfactorily, and I found no especial difficulty. Of the different methods for availability the molybdate went by far the most smoothly, was very satisfactory in fact. Method B gave rather high results on No. 2, but about the same on No. 1. Method C (iron citrate of ammonia-magnesia method) I was not very well impressed with during the course of the analysis, and the results do not check with the others. The last set (as under 3 for total phosphoric acid, without separation of silica) was not included in your list, but I ran them that way for curiosity. The results check pretty well with the others, however, and I think it is much better than Method C.

DISCUSSION OF RESULTS.

Results were received from 11 different analysts. In the determination of the total phosphoric acid the results of the various analysts, with few exceptions, agree fairly well. The average results obtained on total phosphoric acid in the basic slag by the special method (citrate of ammonia-magnesia method) are somewhat lower than when the official method was used. The special method gives results agreeing more closely with results secured after dehydration of the solution and separation of the silica; also with the volumetric method, which is not influenced by the presence of soluble silica. The two methods give results which agree fairly well with each other. The referee is of the opinion that for total phosphoric acid in slags the volumetric method should be used, and there seems to be no necessity for the recommendation of the adoption of the citrate of ammonia-magnesia method.

In the work on available phosphoric acid in both the slag and the mixture of slag and ground rock phosphate the results secured by the various analysts on the molybdate method and on the citrate of ammonia-magnesia mixture method were, as a whole, quite concordant. The two exceptions noted were due to the fact that the analyst allowed the magnesia precipitates to stand overnight before filtering instead of filtering at the end of two hours as called for by the method. The iron-citrate of ammonia-magnesia mixture method applied to the slag in some cases gave considerably higher results than the other two

methods. This is probably due to iron compounds being carried down with the magnesia phosphate precipitate. Some difficulty was experienced by various analysts in getting a complete precipitation of the phosphoric acid by this method. Long continual stirring was necessary before a proper precipitation was effected. It is probable that the difficulty experienced was in a measure due to lack of familiarity with the new method.

It is worthy of note that the molybdate method modified by the use of the official volumetric method gave excellent results in the determination of available phosphoric acid in basic slags (see supplementary results by the California Experiment Station in the table). The referee did not have an opportunity, however, to test this method.

Concordant results have been secured by the so-called molybdate method in the laboratory of the Massachusetts Experiment Station, also in the Coe-Mortimer laboratory by Mr. Whitehouse, by using the ordinary molybdate solution and magnesia mixture which are mentioned in our official methods.

The results of the work on the available phosphoric acid contained in sample No. 2 show conclusively that the Wagner method is perfectly reliable in detecting the adulteration of slags by finely ground mineral phosphates.

In addition to the chemical work which has been done on basic slags during the season, the referee has made a compilation of results of field experiments with different phosphates carried on for the past 14 years at the Massachusetts Agricultural Experiment Station. These tabulated results are offered as a part of the referee's report at this time.

FIELD EXPERIMENTS MADE AT THE MASSACHUSETTS STATION TO COMPARE THE EFFICIENCY OF DIFFERENT PHOSPHATES.

DETAILED DATA.

In 1896 the field was a tough blue-grass sod and had not been plowed for many years. In April it received 600 pounds bone and 200 pounds muriate of potash per acre. After harvesting the grass the field was plowed June 24 and 25 and planted to Longfellow corn. In 1897, May 8, the field was measured off into 13 plots consisting of one-eighth acre each. After the preparation of the soil the following fertilizer schedule was applied to each plot:

Fertilizer schedule.

Ingredients.	Per plot.	Per acre.
	<i>Pounds.</i>	<i>Pounds.</i>
Potash-magnesia sulphate.....	50	400
Nitrate of soda.....	30½	242
Sulphate of ammonia.....	12½	100

In addition to the above the various plots were fertilized as follows:

Special fertilization of various plots.

Plot.	Fertilizer.	Per plot.	Per acre.	Plot.	Fertilizer.	Per plot.	Per acre.
		<i>Pounds.</i>	<i>Pounds.</i>			<i>Pounds.</i>	<i>Pounds.</i>
1	Hoof meal.....	11½	94	7	Hoof meal.....	11½	94
2	do.....	11½	94	8	do.....	11½	94
	Apatite.....	32½	256		Dissolved bone black.....	70	560
3	Hoof meal.....	11½	94	9	Hoof meal.....	11½	94
	S. C. rock phosphate..	47	376		Raw bone meal.....	45	360
4	Hoof meal.....	11½	94	10	Hoof meal.....	11½	94
	Florida soft phosphate.	45½	364		Dissolved bone meal.....	73½	586
5	Hoof meal.....	11½	94	11	Steamed bone meal.....	48½	386
	Basic slag.....	67½	538	12	Hoof meal.....	11½	94
6	Hoof meal.....	11½	94		Acid phosphate.....	90½	724
	Navassa phosphate....	49	392	13	Hoof meal.....	11½	94

The field was planted to corn and harvested per acre as follows:

Corn harvested from plots.

Plot.	Fertilizer.	Corn per acre.	Stover per acre.	Plot.	Fertilizer.	Corn per acre.	Stover per acre.
		<i>Bushels.</i>	<i>Pounds.</i>			<i>Bushels.</i>	<i>Pounds.</i>
1	No phosphate.....	58.5	4,640	8	Dissolved bone black..	61.83	4,384
2	Apatite.....	56.5	3,800	9	Raw bone meal.....	67.33	4,560
3	S. C. rock phosphate...	64.5	4,280	10	Dissolved bone meal...	63.33	4,400
4	Florida soft phosphate...	72.5	4,960	11	Steamed bone meal.....	50.33	3,600
5	Phosphatic slag.....	62	4,960	12	Acid phosphate.....	62.83	4,320
6	Navassa phosphate.....	67.83	4,880	13	No phosphate.....	67.33	4,720
7	No phosphate.....	64.33	4,336				

In 1898 the same amount of fertilizer was applied as for the previous year and the field was planted with Fottler's Brunswick cabbage.

Cabbage harvested from plots.

Plot.	Fertilizer.	Cabbage per acre.	Plot.	Fertilizer.	Cabbage per acre.
		<i>Pounds.</i>			<i>Pounds.</i>
1	No phosphate.....	71,892	8	Dissolved bone black.....	42,920
2	Apatite.....	50,088	9	Raw bone meal.....	49,496
3	S. C. rock phosphate...	48,840	10	Dissolved bone meal.....	43,160
4	Florida soft phosphate...	46,120	11	Steamed bone meal.....	36,836
5	Phosphatic slag.....	47,400	12	Acid phosphate.....	42,440
6	Navassa phosphate.....	45,080	13	No phosphate.....	36,440
7	No phosphate.....	62,440			

In 1899 the fertilizer scheme was as in previous years with the exception that 50 pounds of high-grade sulphate of potash was used per plot instead of 50 pounds of potash-magnesia sulphate. The crop planted was Pride of the North corn.

Yield per acre of corn and stover, 1899.

Plot.	Fertilizer.	Shelled corn.	Stover.	Plot.	Fertilizer.	Shelled corn.	Stover.
		<i>Bushels.</i>	<i>Pounds.</i>			<i>Bushels.</i>	<i>Pounds.</i>
1	No phosphate.....	85.6	5,360	9	Raw bone meal.....	83.6	5,920
2	Apatite.....	82.0	5,520	10	Dissolved bone meal...	81.1	4,160
3	S. C. rock phosphate...	80.1	5,280	11	Steamed bone meal....	69.5	4,000
4	Florida soft phosphate...	82.1	5,600	12	Acid phosphate.....	68.5	4,720
5	Phosphatic slag.....	81.6	5,720	13	No phosphate.....	67.2	5,200
6	Navassa phosphate...	80.3	5,640		Average of no phos- phate plots.....	77.8	5,333.3
7	No phosphate.....	81.1	5,440				
8	Dissolved bone black..	87.9	5,600				

In 1900 the fertilizer scheme was as in previous year. Two crops were grown, Clydesdale oats and Hungarian grass. The two crops harvested per acre as follows:

Yield per acre of oats and grass, 1900.

Plot.	Fertilizer.	Oat hay.	Hunga- rian hay.	Plot.	Fertilizer.	Oat hay.	Hunga- rian hay.
		<i>Pounds.</i>	<i>Pounds.</i>			<i>Pounds.</i>	<i>Pounds.</i>
1	No phosphate.....	5,800	3,800	8	Dissolved bone black..	6,800	3,680
2	Apatite.....	5,880	4,000	9	Raw bone meal.....	6,280	3,800
3	S. C. rock phosphate...	5,800	4,000	10	Dissolved bone meal...	5,760	3,480
4	Florida soft phosphate...	5,560	4,200	11	Steamed bone meal....	5,360	3,440
5	Phosphatic slag.....	6,720	3,840	12	Acid phosphate.....	5,560	3,840
6	Navassa phosphate.....	5,640	3,960	13	No phosphate.....	3,920	3,880
7	No phosphate.....	5,120	3,960		Average, 1, 7, and 13..	4,946.67	3,880

In 1901 fertilizers were applied, and amounts recalculated on basis of analysis to supply equal amounts of phosphoric acid and nitrogen per plot. The nitrate of soda and the potash for this year were applied so as to furnish 50 per cent more actual nitrogen and potash.

Fertilizer schedule, 1901.

Ingredients.	Per plot.	Per acre.
	<i>Pounds.</i>	<i>Pounds.</i>
Sulphate of potash (high grade).....	37.5	300
Nitrate of soda.....	45.5	364
Sulphate of ammonia.....	12.5	100

In addition to this the various plots were fertilized as follows:

Special fertilization of various plots, 1901.

Plot.	Fertilizer.	Per plot.	Per acre.	Plot.	Fertilizer.	Per plot.	Per acre.
		<i>Pounds.</i>	<i>Pounds.</i>			<i>Pounds.</i>	<i>Pounds.</i>
1	Hoof meal.....	12.75	102	8	Hoof meal.....	12.75	102
2	do.....	12.75	102		Dissolved bone black..	67.25	522
	Apatite.....	32	256	9	Hoof meal.....	2	16
3	Hoof meal.....	12.75	102		Raw bone.....	50.50	404
	S. C. rock phosphate..	47	376	10	Hoof meal.....	1	8
4	Florida soft phosphate	45.50	364		Dissolved bone meal..	54	432
	Hoof meal.....	12.75	102	11	Hoof meal.....	1.25	9
5	do.....	12.75	102		Steamed bone meal..	47.50	380
	Phosphatic slag.....	67.25	538	12	Hoof meal.....	12.75	102
6	Hoof meal.....	12.75	102		Acid phosphate.....	47.50	380
	Tennessee phosphate..	37	296	13	Hoof meal.....	12.75	102
7	Hoof meal.....	12.75	102				

Crop of Danvers Yellow Globe onions harvested, 1901.

Plot.	Fertilizer.	Onions.	Scallions.	Plot.	Fertilizer.	Onions.	Scallions.
		<i>Bushels per acre.</i>	<i>Pounds per acre.</i>			<i>Bushels per acre.</i>	<i>Pounds per acre.</i>
1	No phosphate.....	278.5	1,280	8	Dissolved bone black..	209.5	600
2	Apatite.....	222.3	1,840	9	Raw bone.....	252.3	640
3	S. C. rock phosphate..	235.4	1,800	10	Dissolved bone meal..	213.2	600
4	Florida soft phosphate	150.6	2,280	11	Steamed bone meal..	187.8	560
5	Phosphatic slag.....	251.8	1,160	12	Acid phosphate.....	187.8	920
6	Tennessee phosphate..	205.7	1,720	13	No phosphate.....	123.4	1,800
7	No phosphate.....	141.4	2,000				

In 1902 the fertilizer scheme was the same as in the previous year except that 22 pounds of niter lime were added to each plot in July (176 pounds per acre). The crop grown was Danvers Yellow Globe onions.

Yield per acre of Danvers Yellow Globe onions, 1902.

Plot.	Fertilizer.	Sound onions.	Scallions.	Plot.	Fertilizer.	Sound onions.	Scallions.
		<i>Bushels.</i>	<i>Pounds.</i>			<i>Bushels.</i>	<i>Pounds.</i>
1	No phosphate.....	195.7	8,560	8	Dissolved bone black..	173.8	5,640
2	Apatite.....	101.7	8,480	9	Raw bone.....	301.4	4,144
3	S. C. rock phosphate..	121.8	9,360	10	Dissolved bone meal..	338.9	5,400
4	Florida soft phosphate	52.3	6,880	11	Steamed bone meal..	243.8	5,840
5	Phosphatic slag.....	252	5,600	12	Acid phosphate.....	159.4	6,560
6	Tennessee phosphate..	44.6	6,960	13	No phosphate.....	26.2	6,600
7	No phosphate.....	50.5	5,360				

In 1903 the fertilizer scheme was the same as in 1901; the crop grown was Danish Ballhead cabbage.

Yield per acre of Danish Ballhead cabbage, 1901.

Plot.	Fertilizer.	Hard heads.	Soft, leaves, stumps.	Plot.	Fertilizer.	Hard heads.	Soft, leaves, stumps.
		<i>Pounds.</i>	<i>Pounds.</i>			<i>Pounds.</i>	<i>Pounds.</i>
1	No phosphate.....	4,040	9,360	8	Dissolved bone black..	8,392	31,520
2	Apatite.....	3,560	17,360	9	Raw bone.....	11,800	32,440
3	S. C. rock phosphate..	12,040	24,480	10	Dissolved bone meal...	12,760	29,320
4	Florida soft phosphate	3,840	21,840	11	Steamed bone meal....	8,720	28,200
5	Phosphatic slag.....	9,920	28,040	12	Acid phosphate.....	6,200	24,120
6	Tennessee phosphate..	1,720	29,160	13	No phosphate.....	440	8,080
7	No phosphate.....	400	14,120				

In 1904 the fertilizer scheme was the same as in the previous year except that the whole field had an application of 4,675 pounds of agricultural lime. The crop planted was Leaming field corn, which harvested as follows:

Yield per acre of Leaming field corn, 1904.

Plot.	Fertilizer.	Ensilage corn.	Plot.	Fertilizer.	Ensilage corn.
		<i>Pounds per acre.</i>			<i>Pounds per acre.</i>
1	No phosphate.....	41,000	8	Dissolved bone black.....	30,080
2	Apatite.....	40,720	9	Raw bone.....	45,800
3	S. C. rock phosphate.....	40,496	10	Dissolved bone meal.....	41,840
4	Florida soft phosphate.....	28,240	11	Steamed bone meal.....	28,400
5	Phosphatic slag.....	36,440	12	Acid phosphate.....	29,040
6	Tennessee phosphate.....	32,120	13	No phosphate.....	20,240
7	No phosphate.....	32,344			

In 1905 the fertilizer scheme was the same as in the previous year. The crop grown was grass, timothy, red top, alsike clover, common red clover, mammoth red clover. The crop was harvested August 21 and was mostly weeds; not weighed.

In 1906 the fertilizer applied was the same as in the previous year except that plot 2 received no apatite. A crop of hay and rowen was harvested with the following results:

Yield per acre of hay and rowen, 1906.

Plot.	Fertilizer.	Hay.	Rowen.	Plot.	Fertilizer.	Hay.	Rowen.
		<i>Pounds.</i>	<i>Pounds.</i>			<i>Pounds.</i>	<i>Pounds.</i>
1	No phosphate.....	6,600	1,800	7	No phosphate.....	7,000	2,200
2	Apatite (none this year).....	7,520	1,720	8	Dissolved bone black..	6,960	2,240
3	S. C. rock phosphate..	7,440	1,616	9	Raw bone.....	7,120	2,000
4	Florida soft phosphate	7,600	1,504	10	Dissolved bone meal...	7,520	2,552
5	Phosphatic slag.....	7,600	1,600	11	Steamed bone meal....	7,120	2,264
6	Tennessee phosphate..	7,120	1,624	12	Acid phosphate.....	7,080	2,320
				13	No phosphate.....	6,560	1,600

In 1907 the fertilizer was applied as in previous year except that plot 2 received its usual quantity of apatite, which was omitted during the previous

year. Mixed grasses and clover constituted the crop, which harvested as follows:

Yield per acre of hay and rowen, 1907.

Plot.	Fertilizer.	Hay.	Rowen.	Plot.	Fertilizer.	Hay.	Rowen.
		<i>Pounds.</i>	<i>Pounds.</i>			<i>Pounds.</i>	<i>Pounds.</i>
1	No phosphate.....	8,400	400	8	Dissolved bone black..	9,200	488
2	Apatite.....	8,800	504	9	Raw bone.....	9,240	504
3	S. C. rock phosphate..	8,480	496	10	Dissolved bone meal..	9,160	504
4	Florida soft phosphate	8,480	400	11	Steamed bone meal....	8,320	560
5	Phosphatic slag.....	8,360	416	12	Acid phosphate.....	8,040	600
6	Tennessee phosphate..	8,040	328	13	No phosphate.....	7,240	360
7	No phosphate.....	8,160	240				

In 1908 the fertilizer schedule was the same as in the previous year except that plot 2 received 47 pounds of Arkansas rock phosphate in place of 32 pounds of apatite, as in the previous schedule. Cabbage was grown and harvested as follows:

Yield of cabbage, 1908.

Plot.	Fertilizer.	Cabbage.	Plot.	Fertilizer.	Cabbage.
		<i>Pounds.</i>			<i>Pounds.</i>
1	No phosphate.....	3,800	8	Dissolved bone black..	20,080
2	Arkansas rock phosphate.	4,480	9	Raw bone.....	20,240
3	S. C. rock phosphate.....	11,440	10	Dissolved bone meal.....	12,320
4	Florida soft phosphate.....	10,720	11	Steamed bone meal.....	11,440
5	Phosphatic slag.....	19,120	12	Acid phosphate.....	8,280
6	Tennessee phosphate.....	5,600	13	No phosphate.....	1,840
7	No phosphate.....	2,080			

In 1909 the fertilizer schedule was the same as in the previous year; the crop grown was medium early yellow soy bean.

Yield per acre of yellow soy beans, 1909.

Plot.	Fertilizer.	Beans.	Straw.	Plot.	Fertilizer.	Beans.	Straw.
		<i>Pounds.</i>	<i>Pounds.</i>			<i>Pounds.</i>	<i>Pounds.</i>
1	No phosphate.....	1,796	3,220	7	No phosphate.....	1,712	2,272
2	Arkansas rock phosphate..	1,744	3,176	8	Dissolved bone black..	1,672	2,968
3	S. C. rock phosphate.....	1,816	3,384	9	Raw bone.....	1,856	3,088
4	Florida soft phosphate.....	1,836	3,124	10	Dissolved bone meal..	1,908	2,892
5	Phosphatic slag.....	1,840	3,264	11	Steamed bone meal....	1,964	2,676
6	Tennessee phosphate..	1,812	2,620	12	Acid phosphate.....	1,904	2,552
				13	No phosphate.....	1,496	1,784

In 1910 the fertilizer schedule was the same as in the previous year; the crop grown was potatoes, which harvested as follows:

Yield of potatoes, 1910.

Plot.	Fertilizer.	Mer- chantable potatoes.	Plot.	Fertilizer.	Mer- chantable potatoes.
		<i>Bushels per acre.</i>			<i>Bushels per acre.</i>
1	No phosphate.....	286.4	8	Dissolved bone black..	247.9
2	Arkansas rock phosphate	289.3	9	Raw bone meal.....	258.8
3	S. C. rock phosphate.....	264.8	10	Dissolved bone meal....	264.3
4	Florida soft phosphate.....	234.8	11	Steamed bone meal.....	261.9
5	Phosphatic slag.....	245.5	12	Acid phosphate.....	257.2
6	Tennessee phosphate.....	236.4	13	No phosphate.....	214.7
7	No phosphate.....	244.1			

SUMMARY.

Using the average of plots 7 and 13 (no-phosphate plots) as the basis of comparison, and designating the average yield on these plots as 100, the following table No. 1 will show the comparative efficiency of acid phosphate, basic slag phosphate, and dissolved bone black as sources of available phosphoric acid for the crops mentioned.

SUMMARY No. 1.—*Comparative efficiency of phosphates and bone black based on "no-phosphate" plot as 100.*

Year.	Crop.	No phosphate.	Acid phosphate.	Basic slag phosphate.	Dissolved bone black.
1897.....	(Corn.....	100	95	94	94
	Stover.....	100	95	110	97
1898.....	Cabbage.....	100	86	96	87
1899.....	(Corn.....	100	92	110	118
	Stover.....	100	89	108	105
1900.....	Oat Hay.....	100	123	149	150
	Hungarian hay.....	100	98	98	94
1901.....	Onions.....	100	142	190	158
	Scallions.....	100	48	61	32
1902.....	Onions.....	100	415	656	453
	Scallions.....	100	110	94	94
1903.....	Cabbage.....	100	263	330	346
1904.....	Ensilage corn.....	100	110	139	114
1905.....	Mixed grasses largely weeds.....				
1906.....	Hay.....	100	104	112	103
	Rowen.....	100	122	84	118
1907.....	Hay.....	100	104	109	119
	Rowen.....	100	200	139	163
1908.....	Cabbage.....	100	422	976	1,024
1909.....	(Soy beans.....	100	119	115	104
	Bean straw.....	100	125	161	146
1910.....	Potatoes.....	100	112	107	108
	Average for 14 years.....	100	157	219	212

Using the average yield with acid phosphate and dissolved bone black as a standard, and designating the same as 100, the following table will show more graphically the value of the basic slag phosphate as compared with the two dissolved phosphates as a source of available phosphoric acid.

SUMMARY No. 2.—*Efficiency of basic phosphate as compared with the average of acid phosphate and bone black.*

Year.	Crop.	Average of acid phosphate and dissolved bone black.	Basic slag phosphate.
1897.....	(Corn.....	100	99
	Stover.....	100	115
1898.....	Cabbage.....	100	111
1899.....	(Corn.....	100	105
	Stover.....	100	111
1900.....	Oat hay.....	100	109
	Hungarian hay.....	100	102
1901.....	Onions.....	100	127
	Scallions.....	100	153
1902.....	Onions.....	100	151
	Scallions.....	100	92
1903.....	Cabbage.....	100	108
1904.....	Ensilage corn.....	100	124
1905.....	Mixed grasses, largely weeds.....		
1906.....	Hay.....	100	108
	Rowen.....	100	70
1907.....	Hay.....	100	98
	Rowen.....	100	77
1908.....	Cabbage.....	100	135
1909.....	(Soy beans.....	100	103
	Bean straw.....	100	119
1910.....	Potatoes.....	100	97
	Average for 14 years.....	100	111

Considered individually some of the field experiments have not been very positive in showing the efficiency of the phosphoric acid which the various phosphates furnish. The no-phosphate plots in some instances have furnished as good and even better yields than many of the phosphate plots. Especially is this true in the case of plot No. 1, which was used as a farm garden for some years prior to its selection as part of the field for the phosphate experiments. The longer the fields are used for the experiments the better are the conditions for obtaining comparative results, and during the more recent years the yields have been more significant in indicating the efficiency of the phosphoric acid from various sources.

Particular attention is called to the summaries. It will be noted that for only 3 years out of the 14 has the efficiency of basic slag been less than the acid phosphate, and in the average for 14 years with nine different crops it has proved superior as a source of available phosphoric acid to both acid phosphate and dissolved bone black. It seems to the referee that these field experiments, conducted in a careful, scientific way and covering a period of 14 years, furnish reliable evidence of the high availability of the phosphoric acid in basic slag phosphate and emphasize the importance of the adoption of some chemical method which will give full credit to the phosphoric acid contained in this material. The field experiments will undoubtedly be continued, and I hope will serve in the final report of the special committee and in their recommendations as to the final adoption of the Wagner method as official by the association during the year 1914.

CONCLUSIONS.

The results of cooperative chemical work show the Wagner method to be reliable for the detection of adulteration of basic slag. Long-continued field experiments, as well as the Wagner method of analysis, show the uniform availability of the phosphoric acid which a bona fide basic slag carries, and taken together the analytical results strongly emphasize the importance of the provisional adoption by the association of the Wagner method of analysis.

It is therefore recommended—

(1) That the following method of analysis be adopted provisionally by this association pending further study and more complete data in regard to field and pot experiments.

A. *Making the citric solution.*—Weigh 5 grams of the basic slag; transfer to a one-half-liter Wagner flask containing 5 cc of 95 per cent alcohol. The flask should have a neck width of at least 20 mm and be marked at least 8 cm below the mouth. Make up to the mark with dilute citric acid solution (2 per cent) of a temperature of 17.5° C. Fit the flask with a rubber stopper and put at once into the rotary apparatus for 30 minutes, making 30 to 40 revolutions per minute. Take off and filter immediately.

B. *Analysis of the citric solution.*—As soon as the filtration is completed analyze the solution at once according to the so-called molybdate method, which in detail is as follows: To 50 cc of the clear filtrate add 100 cc of molybdate solution made according to the official methods. Keep the beaker in a water bath until the temperature reaches 65° C.; take out and allow to cool at ordinary temperature. Then filter and wash the yellow precipitate of phosphomolybdate of ammonia four or five times with 1 per cent nitric acid. Dissolve in 100 cc of 2 per cent ammonium hydroxid (cold), nearly neutralize with hydrochloric acid, and add to the solution 15 cc of magnesia mixture (made according to the official method) drop by drop during continuous stirring. After 15 minutes add from 10 to 12 cc of ammonium hydroxid solution (specific gravity 0.90), then cover the beaker with a glass cover and allow to stand for

about two hours. Filter the double phosphate of ammonia and magnesia through a tared platinum Gooch crucible, wash six times with 2 per cent ammonium hydroxid, dry, and proceed as is customary for phosphoric acid determinations.

(2) That further work be done with the citrate of ammonia-magnesia mixture method and the official volumetric method, using the Wagner method of making the citric solution of the slag. The referee believes that the official volumetric method will prove a very satisfactory one for the analysis of the citric solution; sufficient work, however, has not been done to warrant its adoption at this time even as a provisional method.

NEUTRAL AMMONIUM-CITRATE SOLUTION.

By A. J. PATTEN and C. S. ROBINSON.

Since the proposal of the ammonium-citrate method for the determination of available phosphoric acid, much trouble has been experienced in preparing a strictly neutral solution of the reagent. The weakness of both the acid and the base renders the end point quite indistinct with ordinary indicators, and much time and patience are required on the part of the operator to obtain the desired results. Several modifications of the simple titration method have been proposed, but each has objections which prohibit its common acceptance by practical chemists. The importance which the method has assumed in agricultural work demands, however, that some convenient means be devised for preparing the necessary solution. Such a method has recently been proposed by Hall and Bell¹ and was later shown by Hall² to be quite suitable for ordinary laboratory use. At the time these articles appeared the authors of this paper were engaged in working out the same method, and the results are here offered, not with the idea of claiming any credit for the development of the method, but simply as corroborative evidence in favor of its general acceptance.

The method of procedure is essentially the same as that followed by Hall. A solution of citric acid was almost neutralized, care being taken to keep the density above 1.09. Small samples of this solution were then titrated with a dilute solution of ammonium hydroxid (about 3 per cent) to determine the approximate amount required to neutralize the remaining acid. Definite quantities of the citrate solution were then removed with a pipette and transferred to clean, dry flasks. To these portions of the original solution varying quantities of the dilute ammonia solution were added in such a way that several contained more and several less than the approximate amount required for exact neutralization, as determined by the titration with corallin. These solutions were then made up to a definite volume and placed in a thermostat, the temperature of which was held constant, and allowed to come to the temperature of the bath, after which their resistances were measured by the Wheatstone bridge method. Plotting the cubic centimeters of ammonium hydroxid added against the bridge readings gave a curve from which could be read the amount

¹J. Amer. Chem. Soc., 1911, 33: 711.

²J. Ind. Eng. Chem., 1911, 3: 559.

of ammonia required to neutralize the acid remaining in a given quantity of the citrate solution. Only one of several titrations by this method is here shown:

Titration curve.

[Temperature, 33.3° C. \pm 0.02. Resistance in box, 5 ohms.]

	Bridge reading.	Ammo- nium hydroxid.		Bridge reading.	Ammo- nium hydroxid.
		<i>cc per 100 cc sol.</i>			<i>cc per 100 cc sol.</i>
No. 1.....	582.25	0.0	No. 5.....	588.50	20.0
No. 2.....	585.25	5.0	No. 6.....	585.75	25.0
No. 3.....	588.50	10.0	Neutral point calculated..	590.75	15.0
No. 4.....	590.75	15.0	Neutral point observed...	590.75	15.0

In order to determine the personal factor in making up the solution by the other methods of determining the neutral point, portions of the citric acid solution were neutralized by the corallin and the purified litmus methods by four laboratory assistants, working independently. The dilute ammonia solution used was kept in a burette inclosed in opaque paper to prevent the reading being taken until the supposed neutral point had been reached. In this way each operation was made independent of the others. Great care was taken that no loss of ammonia occurred during the process. The results are given in the following table:

Amount of dilute ammonia solution used per 100 cc citric acid solution, by four different observers.

Number.	Ammo- nium hydroxid.	Number.	Ammo- nium hydroxid.
	<i>cc per 100 cc sol.</i>		<i>cc per 100 cc sol.</i>
Corallin used as indicator:		Corallin used as indicator:	
P-I.....	12.30	M-I.....	16.00
P-II.....	12.10	M-II.....	15.00
P-III.....	16.20	M-III.....	16.40
P-IV.....	12.70	M-IV.....	16.60
R-I.....	12.00	I-I.....	12.20
R-II.....	12.00	I-II.....	13.60
R-III.....	14.30	I-III.....	19.60
R-IV.....	13.60	I-IV.....	15.90
Purified litmus as indicator:		Purified litmus as indicator:	
P-I.....	15.00	M-I.....	14.00
P-II.....	13.76	M-II.....	15.00
P-III.....	16.00	M-III.....	12.50
R-I.....	15.00	I-I.....	15.82
R-II.....	17.50	I-II.....	15.82
R-III.....	14.00	I-III.....	15.00

The conductivity of some of the solutions was determined and the readings found to fall on the curve at the points to be expected from the quantities of alkali used. The amounts of ammonium hydroxid vary considerably, and in only one case, using corallin, was the exact neutral solution obtained, while with the litmus method one-third of the trials gave a neutral solution. These examples fairly illustrate the difficulty of making an exactly neutral reagent by the methods most commonly in use, and it is quite possible that in many cases the character of the neutral ammonium-citrate solution varies more than in the cases cited, and that considerable error may be introduced in this way.

To ascertain whether or not these differences in the citrate solution would produce marked difference in the results of analyses made with them, several

actual determinations were made. The solutions used were R-II, C, M-IV, and I-III. (See preceding table.) Solutions were carefully diluted to a specific gravity of 1.09 and the determinations were all made at one time so that there could be no variation due to temperature of bath. Determinations were made on two samples of fertilizer, one containing a small percentage of insoluble phosphoric acid and the other a large percentage. The results are given in the following table:

Determinations made to test effect of differences in the citrate solution.

Solution.	Ammonium hydroxid.	Per cent of phosphoric acid.	
		Sample 1.	Sample 2.
	<i>cc per 50 cc sol.</i>		
R-II.....	6.0	2.84 2.81 2.83	8.86 8.82
C.....	7.5	3.74 3.54 3.80	9.80 9.82
M-IV.....	8.3	4.23 4.07 4.21	10.10 9.98
I-III.....	9.8	4.79 4.77 4.90	10.56 10.36

REPORT ON NITROGEN.

By JAMES W. KELLOGG, *Referee.*

At the last meeting committee A recommended that the referee be requested to study laboratory methods for the determination of availability of organic nitrogen. Seven samples were prepared and sent to about 25 chemists who had signified their willingness to take part in the cooperative work. Three methods were suggested to be used, one being the pepsin hydrochloric acid solution method, and the other two the provisional methods outlined in Bulletin 107, Revised, namely, the alkaline permanganate method and the neutral permanganate method. Some time after the samples and methods had been sent out, my attention was called to the fact that the provisional methods had been modified and a large amount of work had been done with these modified methods. This information was received too late to be sent to the analysts taking part, or to change the experiments already begun by suggesting the use of the later methods. Only a few analysts reported results obtained by the methods suggested by the referee, and several called attention to recent modifications of the same. Owing to the late date at which some of these reports were received, and because the methods suggested for trial are not now being used by those who have given this subject more recent study, it did not appear to be advisable to report the same to the association. The alkaline permanganate method, as modified by Jones, has been adopted by the experiment stations of New York, New Jersey, and the New England States, and the neutral permanganate method as modified by Street is being used by some southern analysts.

Inasmuch as the modified methods are receiving more attention than the methods suggested for the year's work, further consideration of the few results obtained did not seem advisable.

It is recommended, therefore, that the study of methods for the determination of available nitrogen be continued and that the alkaline permanganate and the neutral permanganate methods as now used be considered as applied to crude stock and to commercial fertilizers.

A resolution was introduced by E. L. Baker to the effect that the following method for the determination of nitrogen in commercial nitrates be referred to the referee for 1912 for trial, and the resolution was adopted:

Determination of nitric and nitrous nitrogen (Salle, Ann. chim. anal., 1910, 15: 103-105).—To 0.5 gram of the nitrates in a 600-700 cc flask add 200 cc of distilled water, 5 grams of powdered zinc, from 1 to 2 grams of ferrous sulphate, and 50 cc of a 36° Baumé soda solution. In the neck of the flask place some glass wool and connect with the distilling apparatus. Distil off the ammonia and collect as usual in decinormal sulphuric acid and titrate.

REPORT ON POTASH.

By E. L. BAKER, *Referee*.

The potash work this year has been a repetition of that of the past year, with only minor changes in the methods. In order to test thoroughly the applicability of the proposed methods to different materials, three samples were used representing high-grade salts, kainits, and mixed fertilizers. Sample No. 3 was made by mixing weighed amounts of acid phosphate and muriate and contained, theoretically, 4.85 per cent of potash. The following directions were sent to cooperating chemists:

INSTRUCTIONS FOR POTASH WORK, 1911.

Sample No. 1, commercial muriate; sample No. 2, kainit; sample No. 3, acid phosphate and potash. Thoroughly mix samples before use. Potash in each sample to be determined by the official method (Bul. 107, Rev., Bureau of Chemistry) and by the volumetric and gravimetric cobalti-nitrite methods.

VOLUMETRIC METHOD (DRUSHEL'S SLIGHTLY MODIFIED).¹

Sodium nitrite solutions.—Dissolve 220 grams of sodium nitrite in water and dilute to 500 cc.

Cobalt acetate solution.—Dissolve 113 grams of cobalt acetate in about 300 cc of water, add 100 cc of glacial acetic acid, and dilute to 500 cc.

Sodium cobalti-nitrite solution.—Mix equal parts of the sodium nitrite and cobalt acetate solutions a few hours before required for use. A yellow precipitate forms on standing. Filter just before using.

Standard solutions.—Fifth-normal potassium permanganate and fifth-normal oxalic acid; solutions of fertilizers to be made up according to the official method.

Sample No. 1.—Run 10 cc of solution, equal to one-fifth of a gram, from a burette into a porcelain evaporating dish; dilute with about 25 cc of water and add 1 cc of glacial acetic acid; then add slowly, so that the precipitate may not be too finely divided, 15 cc of sodium cobalti-nitrite reagent; evaporate on a steam or water bath to a thick sirup, which becomes just firm on cooling. Care should be taken not to evaporate to dryness. Stir with cold water until excess of cobalti-nitrite reagent has dissolved; allow to settle and decant two or three times through a small funnel containing a perforated porcelain disk and a thick pad of ignited asbestos. Transfer precipitate to filter and wash thoroughly with water.

¹ Chem. News, 1908, 97: 124.

In the meantime an excess of fifth-normal potassium permanganate (about 65 cc) is measured into a 500 cc Erlenmeyer flask, diluted with about 200 cc of water and heated on a hot plate nearly to boiling. To this solution transfer the precipitate and asbestos; mix well by revolving the contents of the flask and maintain at nearly a boiling temperature, stirring frequently. In a few minutes manganese hydroxid separates out and the solution darkens; continue heating with occasional stirring 10 to 15 minutes longer, or until the color of the permanganate disappears and the supernatant liquid becomes clear; then add 5 cc of dilute sulphuric acid (1 to 1), stir, and allow to stand about 5 minutes in order to oxidize the last traces of the potash precipitate; add an excess of fifth-normal oxalic acid (15 cc); keep the solution hot until it becomes colorless and the manganese hydroxid precipitate has completely dissolved, then titrate to color with fifth-normal potassium permanganate.

From the whole amount of permanganate employed, subtract the permanganate equivalent of the oxalic acid used and multiply the remainder by the factor 0.001712, which is the factor for strictly fifth-normal potassium permanganate.

GRAVIMETRIC COBALTI-NITRITE METHOD.

Sample No. 1.—Precipitate precisely as above. Filter through a Gooch crucible, wash thoroughly with cold water and finally four or five times with 80 per cent alcohol. Dry one hour, or until constant weight is obtained, in a steam or water oven.

Multiply weight by the factor 0.2075. Report time required to obtain constant weight.

Sample No. 2.—Measure 25 cc of solution, equivalent to 0.5 gram, into a porcelain evaporating dish, add 1 cc of glacial acetic acid and 10 cc of cobalti-nitrite reagent, and determine potash by the volumetric and gravimetric cobalti-nitrite methods as in sample No. 1, using about 45 cc of fifth-normal potassium permanganate and 15 cc of fifth-normal oxalic acid.

Sample No. 3.—(a) Measure 50 cc of solution into a platinum evaporating dish, add sulphuric acid (1:1) and ignite as in the official method. Transfer to a porcelain evaporating dish with hot water and concentrate to a volume of 5 to 10 cc. Add 1 cc of glacial acetic acid and 10 cc of reagent. Proceed as in sample No. 1, using about 30 cc of permanganate and 15 cc of oxalic acid. (Note. In making up the solution of this sample care should be taken to filter at once after precipitating with ammonium hydroxid and ammonium oxalate and cooling, as long standing of the solution in the presence of the insoluble matter seems to produce higher results.)

(b) Determine potash also by the gravimetric cobalti-nitrite method, using 50 cc aliquot, and by the official method.

MODIFIED OFFICIAL METHOD.

Sample No. 3.—Weigh 2.5 grams upon a 12.5 cm filter paper and wash with successive small portions of boiling water into a 250 cc graduated flask, to a volume of about 200 cc; add 2 cc of concentrated hydrochloric acid, heat to boiling, and precipitate with ammonium hydroxid and ammonium oxalate; cool, dilute to 250 cc, filter, take a 50 cc aliquot equivalent to 0.5 gram, and finish by the official method.

(Note.—Corrections should be made and reported for blanks upon all determinations.)

REMARKS.

The accuracy of the volumetric method depends mainly upon two things: The method of precipitation and the oxidation of the potash precipitate during titration.

To obtain complete precipitation a liberal excess of reagent must be used and strict adherence to the directions for evaporation should be observed. In the case of mixed fertilizers, if the solution is too dilute when the reagent is added, a very finely divided precipitate forms, which is hard to handle. With potash salts the same seems to be true if the solution is too concentrated.

In the titration the oxidation must be complete before oxalic acid is added. The darkening of the permanganate solution is no sign that the yellow precipitate is entirely decomposed, for it requires from 5 to 15 minutes longer time,

depending upon the amount of precipitate present. The disappearance of the color of the permanganate is a fairly good indication that the reaction is completed, although it is well to examine the surface of the solution closely for traces of the yellow precipitate, which can usually be seen if present.

COMPARISON OF THE OFFICIAL, THE MODIFIED OFFICIAL, AND THE VOLUMETRIC AND GRAVIMETRIC COBALTI-NITRITE METHODS.

Cooperative results on potash (percentage).

Analyst.	Sample No. 1.			Sample No. 2.			Sample No. 3.			
	Official meth- od.	Cobalti-nitrite.		Official meth- od.	Cobalti-nitrite.		Official meth- od.	Cobalti-nitrite.		Modi- fied of- ficial meth- od.
		Volu- metric.	Gravi- metric.		Volu- metric.	Gravi- metric.		Volu- metric.	Gravi- metric.	
H. H. Hill, Blacks- burg, Va.	51.37 51.38	51.27 51.36 51.44	¹ 51.33 51.50 ¹ 51.35	13.19 13.20 13.21	13.28 13.20	13.23 13.31	4.49 4.51	4.61 4.60 ¹ 4.56	4.63 4.77 ¹ 4.52	4.67 4.70 4.73
Average.....	51.38	51.36	51.39	13.20	13.24	13.27	4.50	4.59	4.64	4.70
P. L. Hibbard, Berkeley, Cal.	48.93 48.93 49.01 48.50 48.93 49.27 50.15 49.43 48.66 50.54	48.20 49.80	12.40 12.57 12.70	12.95 13.00	4.51 4.53 4.64 4.56 4.51	5.32 5.39	4.80 4.76
Average.....	49.24	49.00	12.56	12.98	4.55	5.36	4.78
P. L. McCreary, Berkeley, Cal.	51.40 51.44	49.20 49.30 49.60 50.20 50.46 50.63 51.48	50.68 51.30	13.26 13.23	13.65	4.55 4.58	4.40 4.40 4.40	4.70 4.72
Average.....	51.42	50.12	50.99	13.25	13.65	4.57	4.40	4.71
O. M. Shedd, Lex- ington, Ky.	51.65 51.57	48.83 48.54 50.82 50.12	52.18 52.40	13.37 13.40	12.70 12.68 13.00 12.99	13.48 13.51	4.52 4.53	4.53 4.51	4.48 4.45
Average.....	51.61	49.58	52.29	13.39	12.84	13.50	4.53	4.52	4.47
Arao Itano, East Lansing, Mich.	51.60 51.60 51.67 51.48	51.19 50.85 50.20 49.91	51.77 51.92 51.25 51.12	13.64 13.60 13.73 13.72	13.01 13.05 13.01 12.98	13.04 13.14 13.49 13.51 13.51	4.67 4.77 4.69	4.41 4.47 4.37 4.30 4.38 4.44	6.27 6.26 6.37 6.29 7.22 7.44 7.42 7.33
Average.....	51.58	50.50	51.51	13.67	13.01	13.36	4.71	4.39	6.82
Cornelius Beatty, College Park, Md.	51.75 51.85 52.35 52.40	51.23 51.62 51.85 52.00 52.14 52.20 52.31 52.36	13.18 13.22 13.23 13.28	10.85 11.06 11.23 11.30 11.30 11.36 11.39 11.47	13.15 13.24 13.30 13.32 13.32 13.35 13.37 13.42	4.69 4.73	3.49 5.17 5.51 5.70	4.61 4.61	4.69 4.69 4.71 4.73
Average.....	52.09	51.96	13.23	11.25	13.31	4.71	4.97	4.61	4.71

¹ Used porous clay crucibles in filtering.

Cooperative results on potash (percentage)—Continued.

Analyst.	Sample No. 1.			Sample No. 2.			Sample No. 3.			
	Official meth- od.	Cobalti-nitrite.		Official meth- od.	Cobalti-nitrite.		Official meth- od.	Cobalti-nitrite.		Modi- fied official meth- od.
		Volu- metric.	Gravi- metric.		Volu- metric.	Gravi- metric.		Volu- metric.	Gravi- metric.	
L. T. Bowser, Day- ton, Ohio.	50.80 51.16	51.74 51.14 51.05 51.23 51.56 50.79	50.90 51.29 50.20 50.90 50.57 50.80	13.09 12.98 13.29	13.44 13.51 13.34 13.30 13.44 13.44	13.31 13.26 13.29 13.39 13.31 13.24	4.58 4.55	4.65 4.74 4.65 4.40 4.51 4.52	6.11 5.84 5.69 5.91 5.79 5.61	4.82
Average.....	50.98	51.25	50.78	13.12	13.41	13.30	4.56	4.58	5.83	4.82
A. H. Allen, Rich- mond, Va.	51.36 51.44	13.52 13.48	4.73 4.71
Average.....	51.40	13.50	4.72
F. D. Fuller and J. H. Roop, La Fayette, Ind.	51.37 51.35	48.12	51.80	13.31 13.21	12.11 11.80	11.84 11.75	4.61 4.63	4.48 4.45 4.40 4.42	6.71 6.95 6.86	4.55 4.70
Average.....	51.36	48.12	51.80	13.26	11.96	11.80	4.62	4.44	6.84	4.63
H. D. Edmond, Storrs, Conn.	51.59 51.65	49.86 49.48	51.83 51.49	13.41 13.38	13.06 12.98	13.64 13.67	4.72 4.77	4.59	4.75 4.68	4.83 4.90
Average.....	51.62	49.67	51.66	13.40	13.02	13.66	4.75	4.59	4.72	4.87
J. M. Bartlett and A. G. Durgin, Orono, Me.	52.12 52.00 51.84 51.72	51.57 51.32 53.46 52.00	50.38 50.26 51.54 52.35	13.24 13.53 13.36 13.56	14.74 14.71 14.26	13.23 13.22 13.29 13.60	4.79 4.70 4.72 4.65	4.74 4.73 4.73 4.80	4.64 4.52 4.52
Average.....	51.92	52.09	51.13	13.42	14.57	13.34	4.72	4.75	4.56
J. C. Jurjenns, Madi- son, Wis., average.	50.78	50.37	50.50	13.53	13.34	13.52	4.78	4.21	6.21	¹ 4.25
G. F. Lipscomb, Clemson College, S. C. ²	51.17	51.00 51.25 51.59 51.25 51.25	51.91 52.07 51.90 50.97 51.01 51.57	13.43	13.12 12.88 12.88 13.16 13.02 13.02 13.17	14.05 14.47 13.91 13.65 13.60 13.94 13.65 13.95	5.14	5.12 5.02 5.12 5.12 5.40 5.12	5.30 5.08 5.36
Average.....	51.17	51.27	51.57	13.43	13.04	13.90	5.14	5.15	5.25
Thos. C. Pinkerton, Philadelphia, Pa.	51.51 51.41 51.22	49.73 49.78	49.39 49.18 49.30	13.31 13.29	12.70 12.60	12.07 12.12 12.37	4.49 4.56 4.60	4.40 4.54	5.25 5.20 5.44 5.38	4.62 4.54
Average.....	51.38	49.76	49.29	13.30	12.65	12.19	4.55	4.47	5.32	4.58
R. M. Pinckney, Bozeman, Mont.	51.72 51.50	47.96 47.08 47.08	48.09 49.28 50.09 49.16 51.36	15.18 14.97	10.55 11.09 10.37 10.75 10.92	10.85 10.94 10.81	5.02 4.81	4.54 4.54 4.50 4.41 4.45	6.94 6.66 6.62 6.97 6.94	4.94 4.82
Average.....	51.61	47.37	49.60	15.08	10.74	10.87	4.92	4.49	6.83	4.88
F. B. Porter, Atlan- ta, Ga.	52.08 52.06 52.14	51.53 50.57 51.36 50.42 50.50 50.93	50.83 50.99 50.26 51.19 50.39 51.34	13.30 13.44 13.38	12.72 12.62 12.39 12.39 13.38	12.14 12.20 12.16 12.18 12.16	4.54 4.57 4.55	4.61 4.58 4.61	4.74 4.87 4.48	4.55 4.59 4.57
Average.....	52.09	50.89	50.83	13.37	12.70	12.17	4.55	4.60	4.70	4.57

¹ Omitted from general average.² Work done by two students under supervision of G. F. Lipscomb.

Cooperative results on potash (percentage)—Continued.

Analyst.	Sample No. 1.			Sample No. 2.			Sample No. 3.			
	Official meth- od.	Cobalti-nitrite.		Official meth- od.	Cobalti-nitrite.		Official meth- od.	Cobalti-nitrite.		Modi- fied of- ficial meth- od.
		Volu- metric.	Gravi- metric.		Volu- metric.	Gravi- metric.		Volu- metric.	Gravi- metric.	
Reported by Paul Rudnick: W. D. Turner, Chicago, Ill.										
							4.56			5.10
							4.58			5.16
							4.56			5.05
	52.15	51.99	52.29	13.60	13.26	13.78	4.56	4.51		5.12
	52.09	51.90	52.21	13.76	13.34	13.64	4.59	4.49		5.18
										5.45
Average.....	52.12	51.95	52.25	13.68	13.30	13.71	4.57	4.50		5.12
E. E. Elm, Chicago, Ill.										
	51.57	51.96	52.19	13.70	13.27	13.63	4.62	4.41		4.95
	51.66	51.45	52.22	13.87	13.34	13.50	4.55	4.24		4.74
	51.59	51.75	52.65					4.48		4.73
	51.42	51.83	52.65					4.40	1	5.21
Average.....	51.56	51.75	52.43	13.78	13.31	13.57	4.59	4.38		4.84
L. S. Walker, Am- herst, Mass.										
	51.36	49.88	51.88	13.37	13.04	13.58	4.69	4.58		4.75
	51.44	50.40	52.21	13.32	13.04		4.77	4.41		4.85
Average.....	51.40	50.14	52.05	13.35	13.04	13.58	4.73	4.50		4.78
A. G. Hogan and L. E. Morgan, Co- lumbia, Mo.										
	51.50	47.60	51.00	12.93	13.17	13.22	4.69	4.19		5.08
	51.30	49.20	51.35	13.07	13.63	13.30	4.63	4.42		4.72
	51.55	47.45		13.02	13.34	13.66	4.72	4.06		6.18
		48.34			13.76					
		48.21			13.64					
		49.02								
Average.....	51.45	48.30	51.18	13.01	13.51	13.40	4.68	4.22		5.32
M. P. Sweeney, Geneva, N. Y.										
	52.26	52.41	52.34	13.24	13.72	12.49	4.59	4.64		4.71
	52.16	52.47	52.27	13.68	13.89	12.87	4.53	4.81		4.71
	52.31	52.29	52.09	13.37	13.27	13.50	4.57	4.88		4.68
	52.28	52.29	52.22	13.44	13.33	12.76				4.59
		52.37				12.91				
Average.....	52.26	52.36	52.25	13.44	13.55	12.85	4.56	4.73		4.68
H. P. Fishburn, Moscow, Idaho.										
	51.86	49.47	49.18	13.84	12.61	13.12	4.78	4.51		4.72
	51.86	48.95	49.13	13.84	12.72	13.06	4.79	4.55		4.82
Average.....	51.86	49.12	49.16	13.84	12.67	13.09	4.79	4.53		4.77
W. L. Whitehouse, Moosic, Pa.										
	51.52	51.27	51.47	13.40	13.42	13.57	4.77	4.73		4.76
	51.55	51.27	51.43	13.38	13.42	13.54	4.77	4.80		4.73
	51.52			13.42	13.42		4.77	4.74		4.78
Average.....	51.53	51.27	51.45	13.40	13.42	13.55	4.77	4.76		4.76
General average.....	51.57	50.31	51.03	13.41	12.91	13.11	4.66	4.55		5.27

1 Omitted from average.

The following results were reported by Mr. B. Apel, Dr. Roemer, Dr. Hansen, and Dr. Kamman, official chemists of the Chamber of Commerce, Berlin, using the platonic and the perchlorate methods for samples 1 and 2 and the perchlorate method for No. 3. "The analyses were made exactly according to the methods prescribed for the laboratories of the potash works. Only the averages are here reported. The various findings agreed well with one another and did not deviate more than 0.1 per cent." Averages: Sample No. 1, 51.45 per cent of potash; sample No. 2, 13.27 per cent; sample No. 3, 4.99 per cent.

These determinations are very interesting as showing the agreement between the German and American methods.

COMMENTS BY ANALYSTS.

H. H. Hill, Blacksburg, Va.: I would suggest that a large porcelain dish be substituted for the Erlenmeyer flask in the cobalt volumetric method. The erlenmeyer when hot is difficult to handle and the precipitate of manganese hydroxid which sticks to the sides is somewhat hard to dissolve, whereas with the open dish it goes into solution easier, the agitation of the solution being better accomplished by the use of a long stirring rod. In this way the oxidation of the potash precipitate is more thorough, the unoxidized particles showing up against the white background. The procedure is also shortened. I would also suggest the use of a porous clay crucible instead of the gooch, as it eliminates any error that may creep in from the use of asbestos. These crucibles may be purchased from any of the leading dealers in chemical apparatus.

J. S. Burd, Berkeley, Cal.: I merely desire to say that it appears to me that the results obtainable by the cobalti-nitrite method vary so greatly with slight changes in the manipulation that I can not conceive that it will prove to be a method which can be used to advantage in an ordinary analytical laboratory. It would seem that the factors causing these variations are of such a nature that they could only be controlled in a research laboratory by elaborate precautions. As at present developed it could not be used in a laboratory where it is necessary to turn out large quantities of work. Again I do not see that there is any great saving either in the matter of cost of reagents or time in the gravimetric method and little, if any, in the volumetric determination, as compared with the platinic chlorid method. The method does not seem to be sufficiently promising from any point of view to justify further work on the part of the association.

O. M. Shedd, Lexington, Ky.: I did not obtain very good results last year on the chlorid and kainit, but excellent results on the mixed fertilizer. The work this year shows the same thing and the only reason I can give for it is the larger amount of potassium present in samples Nos. 1 and 2. I never have thought that this method would always prove reliable when very large amounts of potassium are to be precipitated, due mainly, I believe, to the reagent used not being stable. There are some inconsistencies in my results which I have not been able to account for as yet, for instance, the results obtained on weighing the potassium salt and afterwards titrating the same with permanganate. Along this line I think cooperative work should be done, for it will avoid the error of two separate determinations and at the same time show whether the precipitate has a constant composition. My results seem to indicate that the composition is not constant.

Arao Itano, East Lansing, Mich.: The volumetric cobalti-nitrite method gives lower results than either the official method or gravimetric cobalti-nitrite method. The gravimetric cobalti-nitrite method gives slightly lower results than the official method, except with sample No. 3, in which case higher results were obtained in every instance where the method as outlined was followed. The failure to get results agreeing with the official method on samples 1 and 2 may be explained by the small aliquot portions used.

Cornelius Beatty, College Park, Md.: The gravimetric cobalti-nitrite method gives results which agree with those given by the official method. It takes more time than the official method. Two hours are required to evaporate the excess of the cobalti-nitrite reagent to the required sirupy consistency, but the platinic-acid solution used in the official method can be evaporated in three-quarters of an hour. A part of the precipitate is apt to cling to the porcelain dish. This increases the time necessary to remove it. The precipitate attains constant weight after drying 54 minutes, but if it is weighed after drying 30 minutes the error in weighing a half gram precipitate is less than five thousandths of a gram. Perhaps this method might be modified so that it would be as short as the official method. The principal merit of the method lies in the circumstance that platinum is not used as a reagent, which is important in consideration of the present price of platinum and the work of recovering it.

The results obtained by the volumetric cobalti-nitrite method were not satisfactory. In order to remove the precipitate from the porcelain Gooch crucible, it is best to dry it. If the process of heating the precipitate with the potassium-permanganate solution is performed in a beaker, the porcelain crucible may be

immersed in the potassium-permanganate solution with the adhering precipitate and removed after the determination is complete. The precipitate dissolves slowly in the potassium-permanganate solution. The purple color of the potassium-permanganate solution disappears after one hour. The oxalic acid dissolves the manganese dioxid very slowly. The solution does not become perfectly colorless, but retains a faint pink which is not changed by further additions of oxalic acid.

The gravimetric cobalti-nitrite method is identical with the volumetric cobalti-nitrite method as far as the process of obtaining the precipitate is concerned. After the precipitates are obtained it is easier and quicker to weigh them than to treat them as described in the directions for the volumetric method. The volumetric cobalti-nitrite method has no advantage over the gravimetric cobalti-nitrite method.

L. T. Boucser, Dayton, Ohio: The gravimetric method gives results varying about half as much as the volumetric, the difference between extremes by the latter giving about 2 or 3 per cent per 100 per cent of potash (K_2O), and I note that others quite uniformly secure about the same differences. The acid phosphate and potash give results that are about 30 per cent high on the gravimetric method, which strikes me as peculiar. Taken as a whole, from the standpoint of a chemist, considering the method for the first time (as nearly as I can imagine it), the procedure is not inviting from the point of view of simplicity. There are entirely too many ifs and ands to consider, too many conditions calling for predetermination of the nature of the sample to be examined. All these may be kept in mind easily enough by those of us who have spent several years at trials of the method, but the young analyst or the older one who has always secured good results by the platinum method is apt to indefinitely postpone the use of the cobalti-nitrite procedure.

J. H. Roop, La Fayette, Ind.: In the determination of potash by the gravimetric method, in drying the final precipitates obtained from samples No. 1 and No. 2, two hours were required before constant weight was obtained. In the case of samples No. 1 and No. 3 there is apparently a tendency toward too high results when potash is determined by the gravimetric method, due probably to the presence of some impurities which are not carried away by wash water.

In the case of the gravimetric method on sample No. 3, 50 cc of the solution were measured into a platinum dish and sulphuric acid (1:1) was added before the ammonia was driven off. The results obtained were 7.43 per cent and 7.22 per cent. This part of the method was modified by taking aliquots, evaporating to dryness, and then adding the dilute sulphuric acid. The results obtained are those reported in the table. The presence of ammonia probably caused higher results in the former instances. There seems to be no saving in time by the use of either the gravimetric or the volumetric method as compared with the official method and accuracy is undoubtedly sacrificed for cheapness of reagents.

G. F. Lipscomb, Clemson College, S. C.: The method as outlined in the directions sent out for analysis was first carefully tried, but was found to give such discordant results, uniformly from 3 to 5 per cent lower than the official method (Chemistry Bulletin 107, Revised), that the following modification was made in the directions received: Instead of evaporating the solution and precipitate to a pasty consistency over a boiling water bath, we evaporated the potash solution to about 5 cc on a boiling water bath, then removed the flame and added the precipitating agent, after which the evaporation to a pasty condition was continued with the bath just below the boiling point. The precipitate was bright yellow in color. The precipitate obtained in the manner directed by the referee was always dark colored.

Thos. C. Pinkerton, Philadelphia, Pa.: In addition to the three methods specified, I titrated the precipitate weighed in the gravimetric cobalti-nitrite method. Potassium permanganate was standardized against sodium oxalate, tested as described in Treadwell (translated by Hall, vol. 2, p. 555). The cobalti-nitrite determinations were carried almost to dryness and were a thin paste when cold. The loss of potassium by this method seemed to be in proportion to the amount in the sample, No. 1 showing the greatest loss and No. 3 practically none. I can not account for the high results in No. 3 with the gravimetric method.

F. B. Porter, Atlanta, Ga.: From our limited experience with these methods I should say that they are unsatisfactory on potash salts.

Paul Rudnick, Chicago, Ill.: We find that the results by the volumetric cobalti-nitrite method agree fairly well with those obtained by the official chlor-platinate method, but we get consistently high results by the gravimetric cobalti-nitrite method. This is particularly so in the case of sample No. 3. In this case there is a serious lack of agreement both between the two analysts and among their individual results. I regret that this sample was exhausted before we could locate the source of the trouble. It seems very probable, however, that the presence of acid phosphate is a factor in the difficulty.

We also find that the proposed modified official method gives higher results than the original method; and inasmuch as this proposed modification differs in no essential manner from that in use on phosphoric acid for similar purposes, it seems to me that the association should adopt this modification in justice to the fertilizer manufacturers.

In comparing the official chlor-platinate method with the cobalti-nitrite method as outlined for this work, we are very favorably impressed with the great improvement in the character of the precipitate as a result of evaporating to a sirupy consistency only, instead of to dryness as formerly. The precipitated cobalti-nitrite behaves nearly as well as the chlor-platinate precipitate, except for the fact that it does not settle as quickly.

P. F. Troubridge, Columbia, Mo.: We are all of us disappointed in the cobalti-nitrite method. There is no question but that by continued repetition greater accuracy could be obtained by either the volumetric or gravimetric methods. I feel that a method to become official should be one that a good chemist can secure concordant results by paying careful attention to the descriptions, even if he is not making these determinations continuously. The gravimetric method is no gain in time over the official method and does not seem to me worthy of further consideration. The volumetric method has good possibilities when the details are a little more definitely settled.

ADDITIONAL WORK REPORTED BY COLLABORATING ANALYSTS.

O. M. Shedd: The following determinations were made by first weighing the potassium salt obtained by the cobalti-nitrite method and afterwards titrating the same with fifth-normal potassium permanganate. In drying the salt all were constant in one hour.

Percentage potash determinations—Modification 1.

Method.	No. 1.	No. 2.	No. 3.
Gravimetric cobalti-nitrite method	{ 52.18 52.40	{ 13.48 13.51	{ 4.48 4.45
Average	52.29	13.50	4.47
Volumetric cobalti-nitrite method (on same precipitate as above)	{ 50.69 51.03	{ 13.05 13.07	{ 4.24 4.32
Average	50.86	13.06	4.28

I also made some determinations by evaporating the solution to 5 to 10 cc before adding the nitrite reagent.

Percentage potash determinations—Modification 2.

Method.	No. 1.	No. 2.
Volumetric cobalti-nitrite method	{ ¹ 50.80 ² 50.34 ² 50.17	{ ¹ 13.03 ³ 12.99 ⁴ 13.18
Average	50.44	13.07

¹ 0.20 gram and 20 cc reagent; 0.50-gram and 15 cc reagent.

² 0.10 gram and 15 cc reagent; tenth-normal potassium permanganate and tenth-normal oxalic acid used.

³ 0.50 gram and 20 cc reagent; tenth-normal potassium permanganate and tenth-normal oxalic acid used.

⁴ 0.25 gram and 15 cc reagent; tenth-normal potassium permanganate and tenth-normal oxalic acid used.

The results on Nos. 1 and 2, while low, will average higher when the solution is evaporated to 5 to 10 cc before adding the reagent. On No. 3, on which better results were obtained, this was recommended in the directions. I have a sample of solid sodium cobalti-nitrite that is being sold for these determinations, and it seems to me that if it proves satisfactory it will be of great assistance, as it will do away with the unstable cobalti-nitrite solution.

Thomas J. Pinkerton reported the following results obtained by titrating the gravimetric precipitate:

Comparison of gravimetric method and of titrating the gravimetric precipitate.

Gravi- metric.	Volumetric and gravi- metric.	Gravi- metric.	Volumetric and gravi- metric.	Gravi- metric.	Volumetric and gravi- metric.
49.39	49.47	12.07	12.29	5.25	4.50
49.18	48.53	12.12	12.22	5.20	4.62
49.30	48.79	12.37	12.39	5.44	4.57
				5.38	4.48
49.29	48.93	12.19	12.30	5.32	4.54

R. M. Pinckney also titrated the gravimetric cobalti-nitrite precipitate after weighing. He says: "I am unable to explain why this titration did not agree with those which were titrated before drying." His results are as follows:

Titration of gravimetric precipitate after weighing.

Sample 1.	Sample 2.	Sample 3.
46.7376	10.5459	Lost.
47.6792	10.5802	4.5710
48.1072	10.5117	4.5368
47.8504

McCreary and Hibbard report the following additional work:

P. L. Hibbard: Preliminary tests indicated that correct results were not usually obtained, accordingly the following work was done in the hope of finding some modification that would give good results. The method of handling the precipitate after it is obtained seems satisfactory, except that there appears to be no good reason for diluting the permanganate so much; 100 cc of water makes it easier to handle. The results are much influenced by the length of time of evaporation and the amount of dilution of reagent or volume evaporated. The reagent may be entirely decomposed by heating with water a few hours. Referee's instructions were followed closely except in regard to the volume of water added at the beginning of the evaporation. Blank tests indicated so little that no correction was made for them on either gravimetric or volumetric methods. The filter tubes with precipitates for the gravimetric determination were dried at 100 cc for three hours. A little loss was noted during the second hour, but none in the third hour. Results are given in the order in which obtained, the work extending over about 10 days. If the time of evaporation could be accurately controlled, and if the proper dilution of each sample could be known without previous experiment, it appears probable that accurate results would be obtained; but lacking these essentials, the method must, in my opinion, remain unreliable.

Results on sample No. 1, aliquot used=0.2 gram.

Volume. ¹	Time. ²	Potash (K ₂ O).	Method and remarks.
cc.	Hrs.	Per cent.	
20	2½	48.85	} Both run at same time.
20	2½	48.42	
45	2½	48.93	
45	2½	48.93	} Volumetric cobalti.
45	2½	49.01	
45	2½	48.50	
45	2½	48.93	} All run at same time to determine possibility of securing uniform results by uniform conditions using the same solution.
45	2½	49.27	
45	2½	48.20	
45	2½	49.80	} Gravimetric cobalti.
	Min.		
20	60	50.70	} Volumetric cobalti.
20	60	50.15	
5	50	50.00	
5	30	50.07	}do..... } All run at same time and same solution.
5	30	50.46	
5	30	50.35	
5	30	51.06	} Gravimetric cobalti, very difficult to filter.
5	30	51.30	
5	34	51.14	
5	42	50.80	} Volumetric cobalti—all run at same time and same solution.
5	46	51.22	
	Hrs.		
35	2	50.15	} Volumetric cobalti—all run at same time, following referee's directions as nearly as possible.
35	2	49.43	
35	2	48.66	
35	2	50.54	

¹ Volume=volume of potash solution when reagent was added.² Time=length of time heated in evaporating dish on steam bath.

Previous work showed that more nearly correct results were obtained by decreasing volume and time. The last set was run to see if increased skill and familiarity with the method obtained by practice would enable us to get good results by following the referee's instructions exactly.

Results on sample No. 2, aliquot = 0.5 gram.

Volume. ¹	Time. ²	Potash (K ₂ O).	Method and remarks.
cc.	Hrs.	Per cent.	
25	2	12.40	} Volumetric.
25	2	12.57	
25	2	12.70	
25	2	12.95	} Gravimetric.
25	2	13.00	
	Min.		
5	35	13.16	} Gravimetric.
5	35	
5	35	13.06	} Volumetric; last four all run at once.
5	35	13.18	

¹ Volume=volume of potash solution when reagent was added.² Time=length of time heated in evaporating dish on steam bath.

Results on sample No. 3, aliquot=1 gram.

Vol- ume. ¹	Time. ²	Potash (K ₂ O).	Method and remarks.
cc.	Hrs.	Per cent.	
20	2	4.50	} Volumetric. } All run at same time.
20	2	4.49	
20	2	4.47	
20	2	4.47	
20	2	4.84	
20	2	4.77	} Gravimetric. }
	Min.		
5	30	5.32	} Gravimetric. } All run at same time.
5	30	5.39	
5	30	4.51	
5	30	4.53	} Volumetric. }
5	30	4.64	
5	30	4.56	} Volumetric—run at same time.
5	30	4.51	

¹ Volume=volume of potash solution when reagent was added.² Time=length of time heated in evaporating dish on steam bath.

P. L. McCreary: A number of determinations made on chemically pure potassium sulphate by the volumetric cobalti-nitrite method, adhering closely to the referee's directions, gave low and erratic results and in a general way indicated that the length of time of evaporation and the dilution were important factors to be considered. The following determinations were, therefore, made, varying the volume of the potash solution before addition of the cobalti-nitrite reagent and also the time of evaporation.

Results by the volumetric cobalti-nitrite method, varying volume of solution and time of evaporation.

Sample and volume of solution.	Time.	Potash (K ₂ O).	Remarks
cc.	Min.	Per cent.	
Sample 1—Muriate of potash:			
20.....	90	52.25	} Firm on cooling.
20.....	90	52.25	
20.....	70	52.25	} Thick sirup on cooling.
20.....	70	52.25	
20.....	60	49.20	} Filtrate pink, indicating decomposition of reagent.
20.....	60	49.60	
20.....	60	49.30	
20.....	50	51.23	} Thin sirup on cooling.
20.....	50	51.48	
5.....	35	51.64	} Firm on cooling.
5.....	35	51.64	
5.....	35	50.90	
Sample 2—Kainit:			
5.....	30	13.24	
5.....	30	13.34	
5.....	30	13.27	

At the conclusion of all experimental work the following set of determinations was made according to the referee's directions in order to see whether, after more experience with the method, better results might not be obtained.

Final results on sample No. 1.

Vol- ume.	Time.	Potash (K ₂ O).
cc.		Per cent.
35	1 hour 50 minutes.....	50.20
35	1 hour 50 minutes.....	50.46
35	1 hour 50 minutes.....	50.63
35	2 hours.....	51.48

The results seem to indicate that more nearly accurate and uniform results are obtained using a small volume of potash solution and limiting the time of evaporation. The reagent is decomposed by continued heating, and this decomposition is hastened by dilution. It is necessary to have quite a large excess of the undecomposed reagent present at the conclusion of the evaporation to secure good results. Using small volumes of the potash solution, thus shortening the time of evaporation, tends to produce the desired effect. For any given set of determinations run at the same time under identical conditions of dilution and rapidity of evaporation, fairly concordant, if incorrect, results may be obtained. Certain standard conditions might be found which, if closely followed, would give correct results. It would be, however, very difficult if not impossible to duplicate exactly the necessary conditions from time to time, and as the slightest variations produce erratic results the method in its present imperfect state is not reliable.

Arao Itano reported a modification of the gravimetric cobalti-nitrite method. His comments and results are as follows:

In seeking for some explanation of the high results given by the gravimetric cobalti-nitrite method on sample No. 3, it was found that the precipitate contained some phosphate. It was, therefore, believed that if all the phosphates were removed from the solution before treating with the cobalti-nitrite reagent the results might agree with those obtained by the other methods. At this point all of sample No. 3 had been used, although a quantity of solution was still on hand. This solution had been obtained in the usual way by boiling 10 grams for one-half hour with 300 cc of water. By testing this solution it was found that phosphate was present. Four portions of 50 cc each were placed in beakers and numbered. Nos. 1 and 2 were treated with a small quantity of milk of lime, allowed to stand a few minutes, filtered, washed with water, and the excess of lime in the filtrate removed by precipitating with ammonium oxalate in the usual manner. After filtering and washing with water the filtrate was evaporated to dryness and from this point the method was followed exactly as given. Nos. 3 and 4 were treated with baryta water, filtered, washed with hot water, and excess of baryta removed with sulphuric acid, the filtrate evaporated to dryness, ignited, and from this the method was followed as given.

The following table gives the results obtained as compared with those by the official and volumetric cobalti-nitrite methods:

Potash results on sample No. 3 by three methods.

Official method.	Volumetric cobalti-nitrite method.	Gravimetric cobalti-nitrite method—phosphates removed.
<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
4.67	4.41	4.47 (1)
4.47	4.47	4.38 (2)
4.69	4.37	4.31 (3)
.....	4.30	4.31 (4)
.....	4.38
.....	4.44

The removal of the soluble phosphates in this way, however, is rather tedious, as it requires the filtering and washing of two precipitates. Consequently the following method was adopted:

Weigh out samples and boil with water as usual. Then make slightly ammoniacal, add 5 cc of milk of lime, and allow to stand on hot plate for one hour; cool, make up to volume, and filter. A sample of commercial fertilizer collected in the open market was used for further work.

Potash results on a commercial fertilizer by three methods.

Official method.	Gravimetric cobalti-nitrite method untreated.	Gravimetric cobalti-nitrite method treated.
<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
10.28	11.75	10.49
10.39	11.61	10.49
	12.04	10.41
	12.06	10.42

H. H. Hill, associate referee, has called attention to the fact that the factors for calculating potash from K_2PtCl_6 as found in Bulletin 107, Revised, Bureau of Chemistry, vary somewhat from those calculated according to the latest atomic weights. I have recalculated these factors according to the International atomic weights for 1912 (*J. Amer. Chem. Soc.*, 1911, 33:11), and find they should be as follows:

Potassium platonic chlorid to potassium chlorid, 0.3067; to potassium sulphate, 0.3585; to potassium oxid, 0.1938.

For the sake of uniformity the revised factors should be adopted.

DISCUSSION OF METHODS.

I. VOLUMETRIC COBALTI-NITRITE.

This method has now been studied by the association for three successive years, and though it may appear from the many variable results that we are still far from having a method which will give satisfaction in the hands of the average worker, much progress has been made, many interesting points have developed, and certain questions fundamental to its accuracy have been answered.

A careful examination of the data for each of the past three years shows very close agreement for the mixed fertilizers; but in the case of potash salts there is a decided tendency to low results. This is probably due in part to the inability to precipitate completely the large amount of potash in solution. Several analysts have, however, consistently obtained excellent agreements for all the samples tested, showing that with experience it is possible to obtain concordant results.

In justice to the method I wish to say that I believe for the determination of small amounts of potash in such materials as soils, cereals, etc., it can be used with great accuracy, and for fertilizers and substances high in potash, success will depend largely upon the analyst, practice being an important factor. In its present stage of development the method is rather complicated, requiring many operations and too close attention to minor details to prove attractive for control work. As many of the results have been variable and the comments so generally unfavorable, it does not seem best to continue work on this method until it has been further developed. Investigations are now in progress in several laboratories and it is probable that radical changes will be made which will tend toward greater accuracy.

II. GRAVIMETRIC COBALTI-NITRITE METHOD.

Although this method has also proved more or less variable, it is simpler than the volumetric and requires much less time to complete a series of determinations. Very high results were generally obtained upon sample No. 3, owing

probably to the interference of phosphates, as this sample was composed of acid phosphate and muriate.

Mr. Arao Itano, of East Lansing, Mich., has reported a modification of this method by which he obtained very accurate results. Briefly, his procedure is to throw out the phosphates with milk of lime before precipitating with the cobalti-nitrite reagent. With this improvement the gravimetric method is so promising that I think it deserves further study by the association.

III. MODIFIED OFFICIAL METHOD.

It is well known that the official method of making up the solution does not recover all of the soluble potash present in a mixed fertilizer. Recent investigations have shown that this is probably due to the formation of insoluble potash compounds when samples containing iron, alumina, and phosphates are boiled with water. Several different ways of getting this potash in solution have been tried from time to time, but for various reasons, mainly owing to the use of acid for extraction, they have not met with the approval of the association. The proposed modification of washing a weighed amount of sample upon filter paper with boiling water has been tried for the past two years with very satisfactory results.

In the work of 1910¹ an increase of potash recovered of from 0.1 to 0.3 per cent was quite generally reported; the average for the official method being 4.69 per cent, that for the modified method 4.81 per cent, a difference of 0.12 per cent in favor of the latter. About the same increase has been obtained this year, the averages being 4.66 per cent official and 4.71 per cent modified official—a difference of 0.05 per cent in favor of the modification (theory, 4.85).

Last year¹ the referee made a comparison of the results on 32 different samples by both methods, which resulted very favorably for the proposed modification. Twenty-seven samples gave increased amounts of potash ranging from 0.05 to 0.54 per cent. In one sample there was no difference. Four samples gave slightly less. It often happens that both methods agree, but in the majority of cases the modification gives the highest results; the increase, especially for high-grade goods, being sometimes as great as 0.8 per cent to 0.9 per cent.

The method is more accurate than the official, as it recovers more of the soluble potash and gives results closer to the theory; as it also complies with the laws of those States requiring water-soluble determinations, it seems to the referee that it should be adopted as official.

RECOMMENDATIONS.

It is recommended—

(1) That work on the volumetric cobalti-nitrite method be discontinued until further investigation has simplified it and rendered it of more practical value.

(2) That a further study of the gravimetric cobalti-nitrite method be made by the next referee, in the case of mixed fertilizers, using the modification suggested by Mr. Itano of precipitating the phosphates with milk of lime before adding the cobalti-nitrite reagent.

(3) That the proposed modification of the official method be adopted, and that the official method, Bulletin 107, Revised, page 11, (2) "Methods of Making Solution," be revised to read as follows:

(a) *With potash salts and mixed fertilizers.*—Weigh 2.5 grams of the sample upon a 12.5 cm filter paper and wash with successive small portions of boiling

¹ U. S. Dept. Agr., Bureau of Chemistry Bul. 137, p. 16.

water into a 250 cc graduated flask to a volume of about 200 cc. In the case of mixed fertilizers add 2 cc of concentrated hydrochloric acid, heat to boiling, and add to the hot solution a slight excess of ammonium hydroxid, and then sufficient ammonium oxalate to precipitate all the lime present; cool, dilute to 250 cc, mix, and pass through a dry filter.

In the case of muriate and sulphate of potash, sulphate of potash and magnesia, and kainit, dissolve and dilute to 250 cc without the addition of ammonium hydroxid and ammonium oxalate.

Under (3) "Determination," second line should be changed to read 0.5 gram instead of 1 gram.

On page 12—

(b) *Muriate of potash*.—Acidify 50 cc of the solution prepared according to (2) (a) with a few drops of hydrochloric acid, etc.

(c) *Sulphate of potash, sulphate of potash and magnesia, and kainit*.—Acidify 50 cc of the solution prepared according to (2) (a) with a few drops of hydrochloric acid, etc.

(4) That the factors for calculating potash from potassium platonic chlorid (Bul. 107, Rev., Bureau of Chemistry, p. 12) be revised to read as follows:

(c) FACTORS.

For the conversion of potassium platonic chlorid to potassium chlorid use the factor 0.3067; to potassium sulphate, 0.3585; to potassium oxid, 0.1938.

ESTIMATION OF POTASSIUM AS THE COBALTI-NITRITE.

By W. A. DRUSHEL.

In 1907 and 1908 the writer published three papers¹ on a modification of the Adie and Wood volumetric method for potassium and the application of the modified procedure to fertilizers with less than 10 per cent of potassium oxid (K_2O) and to soils and physiological products. It was shown that with proper care the Adie and Wood gravimetric cobalti-nitrite method under the newly described conditions of precipitation and the modified procedure for the volumetric method for small amounts of potassium both give results fairly accurate and concordant with the results obtained by the platonic chlorid method. In no case, however, in the results obtained and published was more than 0.1 gram of potassium oxid used for a determination. The potassium factor, 0.000856 or 0.000857, for strictly tenth-normal potassium permanganate was derived for the modified volumetric procedure from experimental data and theoretical considerations published in the first paper.

The application of the volumetric cobalti-nitrite process to the estimation of potash in soils and such physiological products as urine, blood, lymph, serum, and milk is fully described in papers just cited.

That the modified volumetric procedure may be applied with a fair degree of accuracy for potassium in small amounts (though in somewhat larger amounts than "1 to 50 parts per million"), contrary to a recently published statement,² is shown by the writer's published results, and has been further verified by the results of V. C. Myers,³ of New York, along physiological lines, and by the results of the referees on soils published in Bulletins 132 and 137 of the Bureau of Chemistry.

¹ Amer. J. Sci., 1907, 24: 433; *ibid.*, 1908, 26: 329 and 555; reprinted in Zts. anorg. Chem., 1908.

² Bowser, J. Amer. Chem. Soc., 1911, 33: 1752.

³ Privately communicated.

Synopsis of referees' reports on total potassium in soils for 1909 and 1910.

Year and number of sample.	Number of determinations made.		General averages in per cent.	
	J. L. Smith gravimetric method.	Volumetric cobalti-nitrite method.	J. L. Smith gravimetric method.	Volumetric cobalti-nitrite method.
1909: ¹				
No. 1.....	11	11	1.503	1.531
No. 2.....	36	26	1.661	1.663
1910: ²				
No. 1.....	13	11	1.854	1.863
No. 2.....	13	10	³ 1.739	1.642
No. 3.....	12	9	1.956	1.951

¹ U. S. Dept. Agr., Bureau of Chemistry Bul. 132, p. 25.² U. S. Dept. Agr., Bureau of Chemistry Bul. 137.³ An erroneous computation reported in Bulletin 137 should read 1.670.

In the report of the association for 1909 it was requested by the referee on potash that the determination be made on sample 1 (potassium chlorid of tested purity) and on sample 2 (a complete mixed fertilizer containing a considerable proportion of organic matter) by the official method and also by the proposed volumetric cobalti-nitrite method. The volumetric method was outlined for the cooperating analysts by the referee, it being recommended that not more than 0.2 gram of sample 1 be used; that 1 gram of sample 2 and 10 cc of the cobalti-nitrite reagent be used for each determination; or that for sample 1 an amount of solution corresponding to not more than 0.2 gram of the sample be used. Nine cooperating analysts reported results, some of which were obtained by introducing slight modifications to the method as outlined. These results have been examined to determine the extreme variations by the two methods and the comparative numbers of determinations reported lying within fairly wide limits of variation.

Extreme variation of results by the official and volumetric cobalti-nitrite methods in 1909.

Method.	Sample 1.	Sample 2.
	<i>Per cent.</i>	<i>Per cent.</i>
Official.....	62.35 to 63.21	3.13 to 3.93
Volumetric.....	61.77 to 63.44	3.30 to 3.90
	60.07 to ¹ 64.44

¹ Obtained by a modification of the prescribed procedure.*Proportion of results lying within the limits specified.*

Method.	Between 62.5 and 63 per cent.	Between 3.6 and 3.85 per cent.
Official.....	12 out of 15.....	10 out of 19.
Volumetric.....	7 out of 31 ¹	14 out of 28.

¹ 10 of these results lying below 62.50 per cent were reported by the same analyst.

A tendency toward low results was frequently observed in the volumetric method, particularly in sample 1. This may be due to insufficient use of sodium cobalti-nitrite in making the precipitation, since this reagent on heating

is partially decomposed by the acetic acid which is present. The writer in developing the method did not consider 20 to 25 cc of the precipitating reagent to be more than a liberal excess for 0.2 gram of potassium (K_2O) when used in the presence of acetic acid, instead of 10 cc, as recommended by the referee. The presence of acetic acid appears to be necessary to produce a filterable precipitate, as was shown by Adie and Wood.

In 1910 it was recommended that potash in samples 1 (commercial muriate), 2 (kainit), and 3 (a complete mixed fertilizer) be determined by the official and the volumetric cobalti-nitrite methods, etc. For the volumetric and gravimetric cobalti-nitrite methods it was suggested that 5 cc of the solution of sample 1, equal to 0.1 gram, be run from a burette into a porcelain evaporating dish, diluted to 20 cc. 1 cc of glacial acetic acid and 10 cc of sodium cobalti-nitrite solution be added, etc.

From the results of 17 cooperating analysts the following table of extreme variations, etc., has been obtained:

Extreme variation of results by official and volumetric cobalti-nitrite methods in 1910.

Method.	Sample 1.	Sample 2.	Sample 3.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
Official.....	50.6 to 53.26	12.28 to 13.73	4.39 to 4.99
Volumetric.....	¹ 49.55 to 55.26	¹ 12.11 to 13.35	¹ 4.26 to 4.91
Reported general average by official method.	51.77	12.73	4.69

¹ One analyst reported considerably lower on samples 1 and 2, 46.1 per cent and 10.27 per cent; one analyst reported 4 per cent for sample 3.

Proportion of results lying within the limits specified.

Method.	Between 51.5 and 52 per cent.	Between 12.5 and 13 per cent.	Between 4.6 and 4.75 per cent.
Official.....	23 out of 42.....	26 out of 36.....	22 out of 37.
Volumetric.....	13 out of 49 ¹	27 out of 49 ²	17 out of 52. ³

¹ Five of these results, all below 51.5 per cent, were reported by the same analyst.

² Seven results below 12.5 per cent reported by same analyst.

³ Eleven results, all below 4.6 per cent, reported by two analysts.

Under "Discussion of results" in Bulletin 137, page 21 (1910), the referee says: "Owing to the use of such a small aliquot the variations in sample No. 1 appear to be greater than the actual error occurring in the determination. In calculation this error is increased ten times. The use of a larger aliquot should be studied." In the conclusions the referee further says: "By the volumetric method, as outlined, the majority of analysts have obtained satisfactory results. * * * Although it is difficult to draw definite conclusions from the data received, from my experience with the method I think that with slight modification an accurate optional method can be developed."

From the writer's experience in developing and applying the volumetric method and from his published results it would appear that it was never intended that the method should be applied in practice to cases where the error in the determination will be increased 10 times in the calculation. It must be admitted that the method has certain inherent difficulties leading to errors, which, however, by proper care in manipulation and proper restriction in the application of the method may be kept within fairly reasonable limits, as has been amply shown by the soil analysts and physiological chemists. Obviously

a method intended for substances running under 10 per cent in potassium (K_2O) when tested on such high-grade potash salts as the muriate should be given the advantage of every care and precaution which would make for accuracy. When a 50 per cent potash salt is so aliquoted that only 5 cc may be used for a determination it requires unusual care in measuring this amount from a burette to avoid the introduction of an appreciable error at this point. An error of $1/40$ cc (not an unusual error for analysts accustomed to gravimetric rather than volumetric work) in the two burette readings necessary in measuring out 5 cc of solution may lead to an error of 0.5 per cent in the final result $(2 \times 1/40 \text{ cc}) \div 5 \text{ cc} \times 50 \text{ per cent} = 0.5 \text{ per cent}$. Is it fair to test a method intended for small amounts of potash on a 50 per cent salt and recommend to the cooperating analysts such a small amount of solution of the salt to be used that in measuring from a burette this amount (5 cc) there is the possibility of introducing in the final result an error of 0.5 per cent due to burette manipulation alone? Would it not have been preferable to have the solution sufficiently dilute so that 25 cc instead of 5 cc subsequently diluted to 25 cc with water would have been measured from the burette?

In the matter of concordance in results reference may be made to the work of Shedd (Bulletin 137, pp. 20-22), who has had considerable experience with the volumetric method, both in soils and in fertilizers.

In the use of the cobalti-nitrite precipitating reagent in the presence of acetic acid care must be exercised to keep an ample excess of reagent present during the evaporation, since the reagent is decomposed by acetic acid at the temperature of the steam bath. At least 15 to 20 cc of the reagent should be used for 0.1 gram of potassium oxid if the precipitation and evaporation are made in the presence of 1 cc of added glacial acetic acid. The results for 1910 on commercial muriate generally run low, and if for 1911 the aliquots for the volumetric process have been made on the basis of 5 cc of the potash solution to 0.1 gram of potassium (K_2O), and not more than 10 cc of the precipitating reagent used in the presence of variable amounts of glacial acetic acid, equally low results may be expected from the use of this method on a 50 per cent potash salt.

In conclusion the writer would suggest that the volumetric method be not rejected by reason of results obtained on a 50 per cent potash salt under conditions not very favorable in the hands of analysts unfamiliar with the method, but rather that it be limited to low-grade potash substances, for which it was originally developed and for which satisfactory results have been obtained by a number of analysts. With a more liberal use of the precipitating reagent and more favorable conditions of manipulation in the hands of analysts familiar with the limitations of the method, reasonably uniform and dependable results should be obtained from the use of the volumetric method in fertilizers containing less than 10 per cent of potassium oxid.

The following paper was presented by the referee on potash, Mr. Baker, at the request of the author.

SOME FEATURES OF THE COBALTI-NITRITE METHOD FOR POTASSIUM.

By LEON T. BOWSER.

The writer has been interested in this method from the first, and in addition to his published work has at hand an accumulation of data which it is purposed to put at the service of the association and its members, believing that an

early solution of the cause of difficulty is more probable with numerous investigators studying it than with only one.

The procedure falls naturally into two divisions, precipitation and titration. The method of precipitation is one first published by W. A. Drushel, and practically no change has thus far been made in it. The titration method is an evolution from that proposed by Drushel, but is quite different from that advocated by the writer. The latter at one time stated, as nearly everyone has seemed to believe, that the titration is defective, but that the precipitation is fairly satisfactory. As will be shown, however, exactly the opposite is the case, and all research should be directed toward the discovery of a satisfactory method of precipitation. The chief causes of difficulty in the present one have been worked out, and will be first discussed, followed by a description of a reliable titration procedure, and lastly will be detailed by a description to work out a satisfactory new precipitation method.

DIFFICULTIES IN PRECIPITATION.

Many have found that dilution of the potash solution, volume of the reagent, presence or absence of acetic acid, time, temperature, and degree of evaporation, and various other conditions produce unexpected changes in the final condition of the precipitate, and with some combinations results are high, with others low. Discussion of the variations due to these minor conditions is useless, however, since there are two major ones entirely overshadowing them in importance. One is the effect of certain metallic salts during evaporation, the other the solubility of the yellow precipitate in solutions of cobalt salts, and in a contrary direction the precipitation under certain conditions of little-known bluish-green cobalt compounds.

Salts of such ordinary metals as iron, aluminum, manganese, barium, calcium, magnesium, and copper, as well as many of the less common ones, are those apt to give trouble. Di-potassium-sodium cobalti-nitrite when heated nearly to boiling (as happens during evaporation) in solutions of such salts, is more or less completely decomposed, leaving a pink solution. With some the reaction is very slow, with others almost instantaneous, but there is a remarkable lack of uniformity about the behavior of the tests carried out as exact duplicates. So serious is this difficulty that under certain conditions it would mean failure to attempt the precipitation of potassium in their presence. Sometimes a fairly accurate result may be attained even in the presence of such salts, but frequently the writer has had duplicate determinations give results, one nearly correct, the other but a fraction of the amount of potash present. This is a serious obstacle to the use of the method, and it apparently can not be avoided when using the evaporation procedure, save by removing all metals except sodium and potassium.

To the fact that the precipitate is more or less soluble in solutions of cobalt salts may be attributed the balance of our difficulties. Shedd, in his second paper,¹ approached, but seemingly did not discover, this feature of the subject. He states that the precipitate is acted on by the acetic acid and water present, but concludes that a large excess of reagent is necessary to keep all the potash in solution, while in reality the action of acetic acid and water at boiling is entirely overshadowed by the solvent action of the cobalt salts resulting from decomposition of the reagent. So far as his tests go, they accord fully with the writer's own observations, but to the fact that the reagent is decomposed by heating to boiling, leaving, it is probable, a mixture of primary salts, is due the principal trouble.

¹ J. Ind. Eng. Chem., 1910, 2 : 379.

Upon adding the reagent to a potash solution in the cold, the yellow triple nitrite quickly precipitates and settles. No sooner does the supernatant solution become thoroughly warmed than it begins to lose its characteristic wine color and assumes a reddish tint changing to purple. As the amount of solution grows less the precipitate disappears, and in many cases there is a stage where but a few grains remain to view. Then as the concentration increases there is a redeposition of the nitrite, and by the time pastiness is reached nearly all is precipitated again, although concealed by the purplish cobalt salts.

Titration of the precipitate at different stages of evaporation confirm fully the fact that at certain times a large part is actually dissolved, and that later it is again deposited. In this case, also, there is a remarkable lack of uniformity; sometimes the action is very complete, at others hardly noticeable. In numerous qualitative tests with various salts of cobalt as well as with the reagent, it was found that sometimes part and sometimes all of the triple nitrite goes into solution upon boiling, while upon cooling there are cases where a considerable part is redeposited, and others where never a trace of the precipitate reappears. With some of the latter a small amount was thrown down, however, by adding alcohol, hence the precipitate is somewhat soluble in cold solutions of cobalt salts.

In the light of these facts part of the irregularities of volumetric results are easily explained. During evaporation some of the precipitate goes into solution, but the degree of solution is not uniform, being influenced by factors too numerous and elusive to control. Evaporation to pastiness, which has been found desirable, leaves variable amounts of cobalt solution, accompanied by a proportionately varying amount of the precipitate, which is subsequently washed away in filtering. This must always produce a loss of potash.

In the opposite direction, under certain imperfectly understood conditions, there is deposited along with the yellow precipitate a bluish-green substance insoluble in water, which subsequently takes up permanganate just as does the precipitate. Shedd has shown that the amount of this substance is variable, and at times equivalent to a very considerable amount of potash. This is the positive source of error, and it depends on whether conditions favor the formation of this bluish-green substance or the retaining of part of the precipitate in the pasty cobalt solution as to whether we have high or low results. It is not improbable that the securing of a result nearly correct is due largely to the balancing of these two sources of error.

TITRATION PROCEDURE.

It has been found, notwithstanding all statements to the contrary, that strictly accurate results are attainable by using as little water as possible, adding permanganate, introducing 5 cc of sulphuric acid (1:1), and then heating just to boiling (stirring constantly meanwhile), decolorizing with oxalic acid, and titrating back with permanganate. Perfect decomposition of the precipitate is always secured, and by keeping the solution well stirred there is no loss of nitrous acid. The time necessary for a complete titration should not exceed three or four minutes.

Since the method of precipitation is faulty, proof of the entire accuracy of this titration procedure could not be shown by titration of precipitations from potash solutions, but the writer has been able to establish it in another way. This reaction and precipitate seem especially designed for the detection and estimation of cobalt, and in a paper to appear later the writer will present

a qualitative test so sensitive that one part of cobalt in twenty million of water can be detected. A perfect precipitation of cobalt is easily attained, and its amount is capable of estimation by means of permanganate; hence, with this source of error entirely eliminated, if there occurred any noticeable deviations the trouble would manifestly lie in the method of titration. A large number of successive titrations has shown that the deviation is exactly the same as that between successive titrations of oxalic acid by permanganate; hence no error is introduced by the use of a small volume of water and the addition of sulphuric acid before heating.

ATTEMPTED IMPROVEMENT OF PRECIPITATION.

It must be confessed at the outset that up to the present the effort to secure a satisfactory substitute for the evaporation procedure has not been altogether successful, but some lines of attack have proved encouraging, and ultimate success appears not improbable. The writer has previously shown that when the reagent is added to a potash solution and the precipitation allowed to stand overnight without heating the amount of potash recovered varies with the time of standing and the concentration of the original solution. The introduction of ethyl alcohol, in addition to throwing down a precipitate too finely divided to allow of proper washing, gives unreliable results. Heating such a solution is entirely inadmissible, as the precipitate is partially decomposed in this way.

The substitution of acid-alcohol (one part 95 per cent alcohol, one part glacial acetic acid) for alcohol as an accelerator of precipitation, as recently described by the writer, gives a better texture of precipitate, but the results are no improvement over those obtained by the evaporation procedure. A quantity of pure, dry sodium cobalti-nitrite was obtained, and a number of trials was given it. A sufficient amount was dissolved in water to make a reagent equivalent to that prepared in the regular way, and acetic acid was added in like amount. As thus made up the reagent gave results, both by the evaporation and the acid-alcohol procedures, that were extremely irregular, although almost invariably too low. Later, however, with a different formula for the reagent, results of considerable promise were secured, which will be described.

From the action of boiling solutions of cobalt salts on the yellow precipitate it appeared that an investigation of their behavior in the cold would be desirable, and qualitative studies were made which gave results both helpful and convincing. The most favorable condition for throwing down a perfect precipitate is when there is a large excess of potassium salts. Nearly although not altogether as desirable is a well defined excess of sodium nitrite, while the presence of a large excess of cobalt is a very decided detriment. The formation of sodium cobalti-nitrite demands very little formality; whenever sodium nitrite is added to a solution of a cobalt salt and acetic acid this reagent is formed, no matter what the ratio of cobalt to sodium nitrite, and there is no necessity for adding enough cobalt to combine with all the sodium nitrite used. When the amount of cobalt is but slightly in excess of that required for complete precipitation of the potash a much better precipitate is secured than when it is in large excess. In fact, with certain excesses of cobalt no yellow precipitate is obtained, but a small amount of a gray one, while with a greater excess precipitation does not occur at all. The conclusion can not be escaped that heretofore a grave error has been made by having too much cobalt present during precipitations.

There are several points of importance regarding manipulation which it would be well to have in mind before discussing the behavior of reagents of

various kinds. In all cases except one (to be described later) it has been found best to place the potash solution in a beaker, most conveniently of 250 cc size, and evaporate until only enough solution remains to moisten the bottom thoroughly. After cooling, and before the reagent is added, the solution is whirled around so as to moisten every place where dried salts are visible. Precipitating in a beaker has the advantage, for volumetric work, that the asbestos and precipitate are thrown back into it, and it is unnecessary to remove what adheres to the walls.

It has seemed the best practice to add the reagent very slowly, with constant agitation of the solution in the beaker. Decidedly higher results are secured if the reagent is added suddenly and agitation carried out afterward. If acid-alcohol or any other accelerator is added it should be allowed to wash down the sides of the beaker, accompanied by frequent agitations. It is well to allow a precipitation to stand about five minutes before adding an accelerator. After a precipitate has been filtered it should be titrated as soon as possible, since a long delay produces a loss of potash. The entire method possesses the merit that it can be carried out with ease and accuracy in artificial light.

In harmony with conclusions from the qualitative tests previously described, several reagents were now prepared which contained but a small amount of cobalt, computations showing that about one-tenth as much as usually employed should be sufficient. Of the many prepared, only two (numbered 5 and 7 of the series) were finally deemed promising enough to justify further work. In addition to those that failed, mention should be made of cobalt nitrite, with which it was hoped to obtain the precipitate tri-potassium cobalt-nitrite, but which gave very poor results. In the preparation of these reagents the potassium present as an impurity in the sodium nitrite precipitates out, and must be filtered off. It should be noted that to a greater or less degree all cobalt salts, especially if in contact with acetic acid, are affected by light, and hence should be kept in the dark. The fact must also be borne in mind that asbestos, no matter how carefully purified nor how free from organic matter, takes up a definite amount of permanganate, which must be allowed for. The same asbestos may be used over and over, but it does not thereby lose its affinity for permanganate.

Reagent No. 5 is prepared as follows: Dissolve 1.9 grams of dry sodium cobalt-nitrite and 19.8 grams of sodium nitrite in water, allow to stand for one hour, filter to remove the precipitate which settles, and make up to 100 cc. By observing the precautions regarding manipulation previously described a number of procedures involving this reagent have given very fair, although not entirely uniform results. These procedures are: (1) Slow addition of the reagent to a potash solution; (2) addition after introducing 1 cc of glacial acetic acid; (3) addition of the reagent followed by 10 cc acid-alcohol; and (4) addition preceded by 1 cc of acetic acid and followed by 10 cc of acid-alcohol. Standing for some time, usually from fifteen minutes to two hours, is required to give a complete precipitation. Precipitates secured in these ways are in general of excellent texture, and give no trouble in filtering and washing.

Some very promising results were also obtained by evaporating the potash solution down to about 5 cc and adding 10 cc of acid-acetone (one part acetic acid, one part acetone), followed as usual by 10 cc of reagent No. 5. An extremely good precipitation results, and filtering and washing is very rapid, but results are usually a little high. Very little time could be devoted to this procedure, but it is worthy of further attention.

Reagent No. 7 is prepared as follows: Dissolve 1.1 grams of cobalt nitrite and 19.8 grams of sodium nitrite in water, allow to stand for some time, filter off the muddy brown precipitate, and make to 100 cc. Some good results were obtained with this reagent by the use of procedures 2, 3, and 4 above. Further attention is justified in this case also, as there are many very good points about the reagent.

Lack of time has prevented exhaustive tests of the many possibilities offered by these reagents, but it seems probable that some of the procedures, or methods evolved from them, will ultimately prove successful. More detailed information regarding any of the points in this paper will be gladly furnished by the writer, and it is hoped that in it may be found some facts that may prove of aid to those interested in the development of the cobalti-nitrite method for potassium.

REPORT ON SOILS.

By J. G. LIPMAN, *Referee*, and G. S. FRAPS, *Associate Referee*.

The referee on soils for 1911 was instructed: (1) To investigate the subject of a more accurate method for humus determinations. (2) To make further studies of the modified cobalti-nitrite method. (3) To continue the study of methods for the quantitative estimation of soil acidity.

In accordance with these instructions the work on humus determinations was undertaken by the associate referee, and the results secured are included in this report.

The work on methods for estimating soil acidity could not be carried out in any satisfactory manner because of the lack of exact and reliable working methods. The referee on soils was led, therefore, to test out certain bacteriological soil-acidity work. Since investigation has not been carried sufficiently far to draw final conclusions, a report of progress is herewith presented, and it is hoped that additional data will be secured for the consideration of this association.

I. BACTERIOLOGICAL METHODS FOR THE ESTIMATION OF SOIL ACIDITY.

By J. G. LIPMAN.

As the culture medium for a host of bacteria and of other microorganisms the soil must possess a suitable reaction. If this condition is met the desirable changes will proceed normally. The organic matter will undergo rapid decomposition, ammonia and nitrates will be produced, and carbon dioxide will be evolved in sufficient amounts to provide for the transformation of relatively inert mineral compounds into available plant food. Moreover, a suitable reaction will make possible the fixation of nitrogen by symbiotic and nonsymbiotic bacteria (azo-bacteria), and the economical utilization of legumes for increasing the store of combined nitrogen in the soil. On the other hand, increasing acidity will retard more and more the fermentative changes in the soil, and the bacteria themselves will dwindle in numbers. Finally the soil may become unfit for the natural growth of higher and lower plants and will cease to yield profitable harvests.

Recognizing these facts in an empirical way, farmers in many lands have adopted the practice of applying various kinds of lime and marl at more or less regular intervals. Such applications serve to neutralize the organic acids that tend to accumulate in cultivated land. In this manner the reaction of the soil is not allowed to become too acid for the activities of the desirable bacteria. However, the farmer is often at a loss to know the exact or even approximate amount of lime required for his land. Excessive applications are not desirable, since they needlessly increase the cost of crop production and may lead to too rapid dissipation of the store of soil nitrogen.

Hence the farmer finds himself obliged to invoke the aid of the soil chemist in determining the lime requirements of his land. Unfortunately, however, the chemist is not in a position to supply the desired information. The methods at his disposal for estimating soil acidity are crude and unreliable, as shown by the experience of members of this association. It is for this reason that the referee on soils was instructed to make further study of promising methods. In searching for methods that might prove more accurate than those already tested, it occurred to him to utilize the soil bacteria themselves as indicators of soil reaction. Since such common organisms as *B. mycoides*, *B. subtilis*, *Azotobacter*, etc., are sensitive to changes in the reaction of the medium, it was not difficult to devise a bacteriological method for the quantitative estimation of soil acidity.* The basis for a method of this sort may be found in the following facts:

(1) Organisms like *B. mycoides* fail to produce characteristic growth in nutrient bouillon when the medium has an acidity greater than 2 per cent.

(2) Additions of acid soil to neutral or slightly acid bouillon may increase the acidity of the medium so as to prevent the characteristic development of the organisms.

(3) By adjusting the quantity of soil necessary to modify the reaction of the medium the acidity of the soil itself may be determined.

In accordance with these facts 10 cc portions of nutrient bouillon were placed in test tubes together with varying quantities of soil corresponding to 0.5 gram, 1 gram, 2 grams, 5 grams, and 10 grams. The tubes were then plugged, sterilized, cooled, and inoculated with *B. mycoides*. It was found that the smaller quantities of soil exercised a depressing effect, and that the larger quantities of soil entirely stopped the growth of the bacteria. A considerable number of soil samples was thus tested, and fairly concordant results were secured. It soon became evident, however, that the depressing effect of the soil might have been due to factors other than acidity. This belief was strengthened by the common knowledge that soil sterilized by heat may for a time become unfit for bacterial growth. Hence a quantity of soil was sterilized by being kept in contact with 95 per cent alcohol for some hours. It was then gently heated to drive off the excess of alcohol and placed in test tubes containing sterilized bouillon. The contents of the test tubes were inoculated with *B. mycoides*. Similar quantities of alcohol-sterilized soil were placed in test tubes containing a solution of mannite and mineral salts and inoculated with *Azotobacter*. Characteristic growths occurred in most of the tubes, and the depressing effects of soil acidity became particularly apparent in the mannite-soil cultures inoculated with *Azotobacter*.

Since this is only a report of progress, no attempt will be made to quote figures. It should be added here, however, that the toxic substances produced in sterilizing soil are partly or wholly neutralized by addition of calcium car-

bonate prior to sterilization. Hence the proposed method may be modified in that the quantity of the bouillon and soil used may be kept constant. On the other hand, variable amounts of calcium carbonates may be added and the effect on the bacteria noted. The data thus far secured seem to indicate that a simple and accurate method could be devised, perhaps, in accordance with the facts noted. For this reason it seems desirable to continue the work in accordance with the suggestions here outlined.

II. REPORT ON HUMUS.

By G. S. FRAPS.

At the request of Dr. Lipman, referee on soils, the writer consented to undertake the work on humus and prepare a report on it. The work of the year was confined to a study of the methods for preparing a solution as nearly as possible free from soil particles. This appears to me to be at present the most important part of the problem. The method of preparing the humus solution is also of importance and should be subjected to study.

The following instructions were sent out to those who had expressed a willingness to cooperate:

DIRECTIONS FOR HUMUS WORK, 1911.

Samples.—Three samples of soil are sent. The sample should be mixed thoroughly before any portion is taken for analysis.

Work outlined.—At present the most important point in the humus estimation is the elimination of the clay. We have, therefore, selected two methods for removing the clay for test. The method of solution is not official, but should give concordant results and is used for convenience.

Preparation of solution.—Digest 20 grams of the soil for five hours with 400 cc of fifth-normal hydrochloric acid. Filter on a fluted filter and wash thoroughly. Cover and allow to drain overnight. Measure out 1,000 cc of 4 per cent ammonium hydroxid (1 cc=11.55 cc fifth-normal hydrochloric acid), and wash the soil into a glass-stoppered bottle, digest for twenty-four hours with shaking every hour during the working day, and let settle twenty-four hours. Decant about 800 cc through a folded filter into a dry glass-stoppered bottle and use aliquots of the solution for analysis. Shake the bottle well before withdrawing portions for analysis.

(a) *Official method.*—Evaporate 100 cc to dryness in a platinum dish, dry for four hours in a boiling-water oven, and weight. Ignite and weigh again. Report loss on ignition and ash.

(b) *Mooers-Hampton method.*—Evaporate 100 cc to dryness in a porcelain dish and heat for two hours on a water bath. Take up with five or more successive portions of about 20 cc each of 4 per cent ammonium hydroxid and decant into another dish. Evaporate again, heat as before, take up with ammonium hydroxid, filter into a platinum dish, and wash. Evaporate the filtrate to dryness and complete as in method (a).

(c) *Rather method.*—Place 130 cc in a glass-stoppered cylinder and add 0.65 gram of ammonium carbonate. Allow to stand overnight, filter through a dry filter into a dry flask, and measure out 100 cc for evaporation in the platinum dish. Complete as in the official method.

Remarks.—Please express your opinion in regard to the three methods and give us the benefit of any other observations concerning the matter. An early report will be appreciated.

G. S. FRAPS, *Associate Referee,*
College Station, Tex.

RESULTS OF THE WORK.

The results on humus are reported in Table 1 and those on humus ash in Table 2.

TABLE 1.—Percentage of humus in soils.

Analyst.	Sample No. 1.			Sample No. 2.			Sample No. 3.		
	Official.	Mooers and Hampton.	Rather.	Official.	Mooers and Hampton.	Rather.	Official.	Mooers and Hampton.	Rather.
W. T. McGeorge, Honolulu, Hawaii.....	5.02	0.75	0.87	0.30	0.25	0.27	0.46	0.30	0.25
	5.39	.83	.86	.34	.27	.28	.51	.32	.24
N. C. Hamner, Texas.....	5.47	.67	.67	.33	.32	.32	.33	.28	.28
J. B. Rather, Texas.....	5.00	.65	.66	.24	.29	.22	.24	.20	.26
K. W. White, Pennsylvania.....	.93	.75	.80	.22	.19	.27	.22	.17	.27
	.84	.74	.81	.25	.21	.31	.22	.16	.28
G. W. Walker, Minnesota...	3.26	.74	.61	.28	.29	.14	.32	.32	.17
W. B. Ellett, Virginia.....	5.4380	.4524	.31	.00	.40
	5.03423500
C. S. Robinson, Michigan.....	4.40	.47	.78	.20	.25	.23	.26	.26	.26
	4.57	.55	1.02	.21	.27	.22	.26	.27	.25
	4.73	.59	1.0124	.27	.24
	4.73	.50	.7124	.26	.26
H. C. McLean, New Jersey...	5.52	.77	.71	.30	.39	.22	.37	.30	.27
	5.49	.75	.76	.27	.36	.23	.37	.33	.26
	5.02	.7526	.2538	.29
	5.11	.7127	.2535	.24
24
24
28
E. Van Alstine, Illinois.....	5.03	1.07	.67	.24	.42	.19	.34	.40	.26
	5.24	.95	.73	.16	.50	.14	.39	.46	.23

TABLE 2.—Percentage of humus "ash" in soils.

Analyst.	Sample No. 1.			Sample No. 2.			Sample No. 3.		
	Official.	Mooers and Hampton.	Rather.	Official.	Mooers and Hampton.	Rather.	Official.	Mooers and Hampton.	Rather.
W. T. McGeorge, Honolulu, Hawaii.....	34.00	0.17	0.14	0.38	0.30	0.41	1.15	0.22	0.20
	34.59	.26	.14	.47	.32	.50	.50	.37	.28
N. C. Hamner, Texas.....	37.01	.18	.47	.29	.36	.18	1.45	.33	.38
J. B. Rather, Texas.....	33.00	.33	.24	.25	.49	.22	1.22	.40	.22
J. W. White, Pennsylvania...	.68	.33	.27	.33	.13	.29	.46	.13	.41
	.68	.32	.30	.34	.12	.29	.46	.13	.42
G. W. Walker, Minnesota.....	24.88	.79	.16	.32	.30	.34	1.20	.55	.23
W. B. Ellett, Virginia.....	39.0928	.4547	1.9050
	38.9342	1.8800
C. S. Robinson, Michigan.....	28.95	.45	.51	.40	.39	.29	1.36	.41	.47
	28.83	.48	1.00	.39	.41	.28	1.36	.44	.44
	29.03	.48	1.96	1.32	.45	.50
	29.11	.44	.32	1.33	.45	.53
H. C. McLean, New Jersey...	33.40	.48	.09	.18	.00	.24	1.40	.40	.27
	33.18	.53	.14	.20	.04	.26	1.31	.30	.23
	33.81	.3133	.07	1.53	.33
	34.61	.3833	.14	1.48	.34
13
14
20
E. Van Alstine, Illinois.....	36.27	1.47	.44	.37	.73	.27	2.22	1.12	.46
	35.59	1.16	.27	.34	.72	.30	2.11	.98	.51

REMARKS OF ANALYSTS.

W. P. Kelly, Honolulu: The determinations reported were made by Mr. William T. McGeorge, of the department, who comments on the methods as follows: "Either the Mooers-Hampton or the Rather method gave satisfactory results, both as regards humus and humus ash. The Rather method can be worked in a little less time than that of Mooers-Hampton, but either is satisfactory for such soils as these. The official method is entirely unreliable with heavy clay soils." I may add that neither the Mooers-Hampton nor the Rather method, when applied to such soils as ours, effects a complete removal of the clay.

N. C. Hamner, Texas: The Rather method I consider best, as it is quickest and gives a very low ash, while the Mooers-Hampton has to be evaporated at least twice and the residue extracted several times; even then, in my judgment, it loses a part of the humus originally extracted from the soil occluded by the clay. The agreement between the Mooers-Hampton and Rather methods is very satisfactory, but certainly in No. 4671 the lime was not all extracted, nor was all organic matter.

J. B. Rather, Texas: All lime was not removed from sample No. 2 by the acid. Fresh or tested ammonia solutions should be required.

William Frear, Pennsylvania: The results obtained by the first three methods reported represent as exact a following of the details of the procedure indicated by you as was possible. Mr. White notes that in No. 2 the quantity of carbonate of lime was so great that it neutralized most of the acid used for the removal of calcium and magnesia from their humic combination prior to the alkaline treatment. Supplementary to the results by your methods are duplicates by the use of the Chamberland tube method. This gives results more closely approaching those of the Mooers-Hampton method than do the results secured by the other two methods named, so far as the ash constituents are concerned, although in the case of samples Nos. 2 and 3 the ash in the Chamberland filtrate is higher than the Mooers-Hampton method yielded. The same is true of the organic portion of the filtrate in these two cases. [In reply to a subsequent letter, Dr. Frear wrote:]

I note your comment on the low ash report by Mr. White. Thereby hangs a detail. Mr. White has been working on allied questions for two or three years and has endeavored to diminish the ash by awaiting patiently the subsidence of the suspended mineral matter prior to filtration. Other factors in the results seem not to have been materially changed by this practice, but the elimination of clay as a source of ignition and loss has been largely accomplished. I do not believe, however, that this method would solve the difficulty in case of certain soils, such as the Cuban soils, whose behavior led me a decade ago to the suggestion for the need of improved water-soluble alkaline-humus method to eliminate the error due to the water of hydration contained in the mineral materials taken into the filtrate.

Results by the Chamberland tube method.

Sample.	Humus.	Ash.
	<i>Per cent.</i>	<i>Per cent.</i>
No. 1.....	0.67	0.26
	.70	.26
No. 2.....	.22	.23
	.20	.24
No. 3.....	.25	.16
	.24	.17

G. W. Walker, Minnesota: In making the determinations for humus I have carefully followed your directions. In regard to the preparation of the solution, it would seem to be preferable to weigh out sample of soil on filter and leach with hydrochloric-acid solution until the filtrate gives no test for lime, as I find that unavoidably clay passes through the filter in filtering and washing as you direct. Also in using a fluted filter there is some difficulty in washing free from soil on transferring to flask for treatment with ammonia solution.

As to the three methods for making the determination, I am very well pleased with the Rather method. It appeared to give very good results as far as the removal of clay is concerned. It occurs to me, however, that possibly some of the humus or albuminous matter in the humus might be precipitated by the ammonium carbonate along with the clay. On the whole, it appears to me that the Rather method is an excellent modification of the official method, and, if adopted, would no doubt lead to more accurately comparable results.

Along with the results obtained by the methods you have given, I have tabulated the figures obtained by running the solution in a centrifuge at the speed of approximately 1,500 revolutions per minute.

Results obtained with the centrifuge.

Sample.	Humus.	Humus ash.
	<i>Per cent.</i>	<i>Per cent.</i>
No. 1.....	2.91	18.47
No. 2.....	.23	.43
No. 3.....	.24	.65

C. S. Robinson, Michigan: It was found that after standing 24 hours there was still a large amount of clay suspended in the solution to be used for analysis. The effect of this is shown in the amount of ash in samples Nos. 1 and 3 by the official method, which uses this solution directly for the determination. In both cases the amount of ash obtained in this method was much higher than in either of the other methods. In sample No. 1, which gave the largest amount of suspended matter, the humus results are much higher than the results with the other two methods. This is due, in all probability, to the driving off of the moisture from the ash. On the other hand, while the quantity of ash obtained by the official method in sample No. 3 is approximately three times as great as that obtained by either of the other methods, the average amount of humus is less than that obtained by the Mooers-Hampton and just equal to that obtained by the Rather method. This may, of course, be accounted for by the assumption that the water-holding capacities of the two kinds of ash differed. In sample No. 2 the supernatant liquid was fairly clear, and the effect of the ash was not so marked.

As to the relative merits of the three methods, both the Mooers-Hampton and Rather methods seem to be preferable to the official method. Between the first two there is but little choice though the Rather method requires a little less time on the part of the operator.

The writer is of the opinion that a considerable error may have been introduced into all of this work by the method of preparation of the solution. After filtering the soil from the acid solution it was found quite difficult to remove it from the filter paper without either contaminating it with fibers of the paper or leaving some soil on the paper. It would seem better to follow the official method in this respect or to follow one similar to that which has been in use in this laboratory for some time in the volumetric determination of phosphoric acid. By the latter method the soil would be filtered from the acid solution through a pad of ignited asbestos formed on a perforated porcelain plate placed in a common glass funnel. When the soil has been thoroughly washed the porcelain plate, asbestos, and sample can be easily transferred to a wide-mouthed, glass-stoppered bottle for digestion with alkali. This prevents any possibility either of losing any of the sample or of adding organic matter to it from the filter paper.

H. C. McLean, New Brunswick, N. J.: The first results, in each case, were obtained before becoming accustomed to the methods. The Rather method seems to me to be the best, as it is short and eliminates the clay better than the Mooers-Hampton method. The results seem to correspond very well with the Mooers-Hampton method also.

J. H. Pettit, Urbana, Ill.: Mr. E. Van Alstine, of this station, has done this work. He has no particular comment to make upon the relative value of the methods, and I may say that the results go far to confirm us in the idea that the determination of humus in soils is extremely unsatisfactory. We feel that so far as our work is concerned the determination of one definite constituent of

all organic matter, as, for instance, carbon, is a much better indication of what the soil contains. We, of course, realize that the percentage of carbon varies in organic compounds, and that the relative amounts of these various organic compounds are not always present even in the same soil.

CONCLUSIONS AND RECOMMENDATIONS.

The present official method for humus is very inaccurate on some soils, on account of the clay carried in suspension. Both the Mooers-Hampton and the Rather methods are much more nearly correct. The Rather method is more rapid than the Mooers-Hampton. The centrifuge method, as reported by Mr. Walker, does not remove the ash. The subsidence method, tested by Mr. White, is slow, and I am inclined to think with Mr. Frear that it will not be effective on some soils. It is possible that in the Chamberland tube method, tested by Mr. White, some humus does not pass through the tube.

The associate referee recommends further study of the Rather method with a view to its adoption as an official method by this association. The present official method should be abandoned, as it does not remove all the clay.

The referee then presented the following paper on behalf of the author:

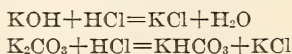
DETERMINATION OF CARBON DIOXID IN SOILS.

By LEON T. BOWSER.

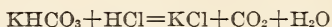
In his 1909 report¹ on carbonates in soils the associate referee tentatively suggested that a volumetric method for the purpose would be desirable and might ultimately be found. The present one, at that time in an advanced stage of development, has since been perfected to the point where it is believed it can be used by nearly any analyst. It is based on one described by J. C. Mims,² and the procedure is essentially that of releasing carbon dioxide by means of hydrochloric acid, absorbing it in a strong alkaline solution, and measuring its amount by titration with a standard acid.

Absorption is accomplished in a tower especially designed to meet the conditions. No preliminary guard tubes are necessary, and instead of rigidly excluding water from contact with the potash solution it is the practice to distill over a small amount, thus insuring the mechanical carrying over of residual carbon dioxide along with the water vapors. Estimation of the amount of carbon dioxide absorbed is accomplished, as before stated, by titration with a standard acid.

Previous to titration the absorbent solution contains a mixture of potassium hydroxid and carbonate. In titrating with an acid, using phenolphthalein as indicator, disappearance of the pink color marks the point at which all hydroxid has been neutralized and the normal carbonate has been converted to bicarbonate, or, in other words, the normal carbonate has been half neutralized:



The titration being continued, after adding a drop of methyl orange, appearance of the usual acid reaction denotes complete neutralization of the bicarbonate:



¹ U. S. Dept. Agr., Bureau of Chemistry Bul. 132, p. 30.

² *Ibid.*, Bul. 65, p. 156.

The volume of acid used in this latter titration, then, is just one-half of that required to release all the carbon dioxide from the condition of a normal carbonate. It follows that 1 cc of normal acid used in the titration between the two end points is equivalent to 0.044 gram of carbon dioxide.

The form of apparatus used is shown in figure 2; F is a flask in which the carbonate is decomposed by an acid, which is introduced through a small separatory funnel, S, or the substitute shown in figure 2, b. The condenser, C, is so constructed that the inner tube is quite short and of small bore. All tubing used in the apparatus, except the body of the tower, is of 2 mm internal diameter, which allows very little space for carbon dioxide to collect and possibly

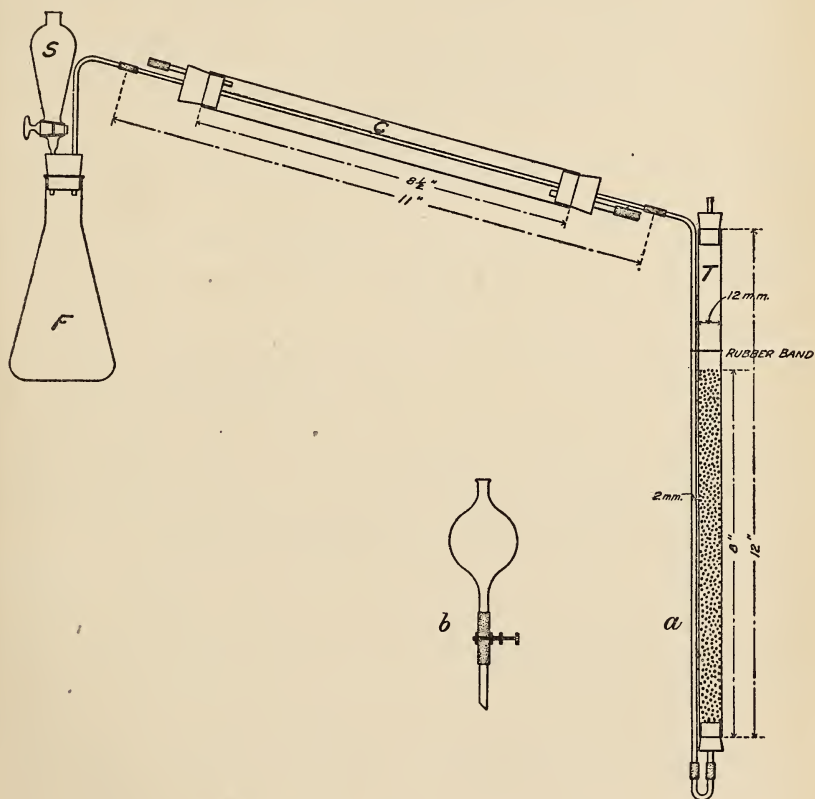


FIG. 2.—Apparatus for determination of carbon dioxide in soils.

escape absorption. Complete details of the construction and dimensions of the absorbing tower, T, are given in the figure.

A suitable amount of soil, usually about 10 grams, is placed in a 100-cc Erlenmeyer flask, then about 50 cc of water is added. The apparatus is connected up, 10 cc of absorbent solution (50 grams of potassium hydroxid in 100 cc solution) pipetted into the tower, and sufficient hydrochloric acid introduced through S to decompose all the carbonates in the flask. With very effervescent soils the acid is let in a few drops at a time; with others the entire amount is added at once. After active effervescence has ceased the flask is heated, taking

care not to force bubbles through the tower too fast, and water is allowed to distil over until the tower is nearly filled.

The carbonated solution is then transferred to a 100-cc volumetric flask, the tower thoroughly rinsed into the flask, and the contents of the latter made up to volume. A 25-cc aliquot is pipetted out and placed in a 250-cc beaker. A few drops of phenolphthalein are added, followed by 10 to 15 cc of 95 per cent alcohol, then acid of approximately normal strength is run in until the color begins to dim, after which decinormal acid is used to complete the discharge of the pink color. The burette reading is recorded, a drop of methyl orange added, and the titration continued to the usual end point. The latter burette reading is set down, and after subtracting the equivalent of carbon dioxide in the reagents the difference in cubic centimeters between the two, multiplied by the factor 0.0044 for strictly decinormal acid, gives the grams of carbon dioxide in the aliquot, from which the percentage in the original sample may be easily found. The amount of carbon dioxide in the reagents is ascertained by a blank determination carried out in the same way as the regular one.

Soils containing 0.1 per cent or less of carbon dioxide require for titration an acid of a strength not exceeding fiftieth-normal, since when stronger ones are used the carbon dioxide is equivalent to but a fraction of 1 cc and too great an error is thus introduced. An occasion may arise where a centinormal acid is demanded, although the writer has never encountered such a case. Even with fiftieth-normal acid much care is necessary in observing end points, and the use of comparison solutions is advisable.

It is probable that the titration will be found the most difficult point in the use of the method. Ordinarily the phenolphthalein end point is supposed to give no trouble, but it is very apt to do so nevertheless. The writer has discovered that the addition of a small volume of ethyl alcohol, after introducing phenolphthalein, totally eliminates all such difficulties, but without this precaution it is improbable that a satisfactory end point can be secured. During this part of the titration the solution should be kept rotating vigorously, since any local excess of acid would carry the reaction on to the point of releasing carbon dioxide from the bicarbonates in the immediate vicinity.

In the addition of methyl orange not more than one drop should be added to 25 cc of the carbonated solution. When this amount is used the change of color is quite easily noted, but the presence of larger quantities renders the observation a matter of difficulty. The end point to observe is when the clear lemon yellow of the alkaline solution becomes a shade darker from the admixture of the pink of the acid reaction just beginning to take place. When the acid used for titration is no weaker than decinormal the color change is plainly noticeable, but with acids more dilute it is advisable to have at hand a comparison solution of the same tint as the titrated solution when alkaline, and the slightest difference of color is then easily noted, in a good light. Even thus, a considerable amount of care must be exercised should an acid as dilute as hundredth-normal be in use, but even this end point is distinguished with accuracy.

The very best of results were obtained on chemically pure carbonates by this method, but for the present paper only the results on soils will be given. As a preliminary experiment two determinations were made on a sort of artificial soil containing a known amount of carbon dioxide. A very pure sea sand was ignited for some time to remove all organic matter and decompose such calcium carbonate as might be present. This was cooled and to a weighed portion was added enough analyzed calcium carbonate to give exactly 0.05 per cent

of carbon dioxid. A blank determination was first made on the water, reagents, and freshly ignited sand, then two determinations were carried out on the artificial soil. The blank first obtained was deducted from the titration results, and the carbon dioxid was calculated from the difference. The determinations gave 0.043 and 0.048 per cent carbon dioxid, an average of 0.0455 as against the 0.05 per cent actually present, which seemed very satisfactory.

There was available a quantity of each of the two samples sent out for the 1909 association soil work, and advantage was taken of the fact to compare this method with the gravimetric one. Four determinations were made on each of these soils, under conditions parallel to those used by the association workers, and the results are given in the table, accompanied by a comparison with the figures obtained by the gravimetric method. The averages given in the association report are: Soil 1, 0.081 per cent; soil 2, 0.027 per cent carbon dioxid, but these include the results of only five analysts, two others reporting too late to be considered. For the present comparison all of the results are taken into account, giving the averages as shown.

Comparison of averages by the volumetric and the association (gravimetric) methods.

Method.	Soil 1.	Soil 2.
Volumetric method.....	0.080	0.026
	.077	.031
	.075	.031
	.084	.026
Average for volumetric method.....	.079	.028
Average for association (gravimetric) method.....	.078	.028

The agreement between the revised association averages and the volumetric method is very close, and shows that the latter is thoroughly reliable. On the score of consistent results the volumetric method is decidedly superior to the gravimetric, the variations between duplicates being only about one-third as great.

Equally favorable results have been secured on routine samples, and no difficulty has ever been experienced in getting good duplicates. The writer believes that a thorough trial of the method by the association will show that it is very accurate, that the results are uniformly concordant, the manipulation is simple, and the apparatus easily constructed and not in the least fragile. These advantages, coupled with the fact that there are very few precautions to be observed, should make it of great service in soil analysis. A more detailed description of the method and the results secured by it will appear a little later in one of the periodicals.

NOTE ON POT EXPERIMENT SHOWING GAINS IN NITROGEN WHEN CERTAIN LEGUMES WERE GROWN.

By B. L. HARTWELL and F. R. PEMBER.

The following table shows the net gain in nitrogen per pot 12 inches in diameter during a five-year pot experiment in which, without nitrogenous manuring, the legumes mentioned below were grown each summer and har-

vested; whereas, in the winter, vetch was grown in the greenhouse in all the pots and mixed with the soil at blossoming time:

Name of crop.	Pot number.	I.	II.	Oven-dry crops removed in five years.	Average per cent of nitrogen in the same.	III.	Per cent of nitrogen in dry fine soil at end (0.1502 per cent at the beginning).	IV.	V.	Net gain in nitrogen during the experiment (V-II).
		Nitrogen in soil at the beginning. (The variation is due to different proportions of pebbles.)	Nitrogen in soil at beginning and in added seeds and water, not including that in vetch.			Nitrogen in the aerial portion of the summer legumes removed.				
Soy bean.....	¹ 1	Grams. 30.20	Grams. 35.68	Grams. 346	P. ct. 3.10	Grams. 10.73	P. ct. 0.1994	Grams. 40.10	Grams. 50.83	Grams. 15.15
	² 2	29.43	34.91	351	3.07	10.76	.1992	39.03	49.79	14.88
	3	29.43	34.91	362	3.10	11.22	.1995	39.08	50.30	15.39
	4	30.01	35.50	357	3.10	11.07	.1967	39.30	50.37	14.87
Adzuki bean.....	5	29.33	32.23	190	2.58	4.91	.1887	36.85	41.76	³ 9.53
	² 6	29.89	32.79	203	2.24	4.55	.1913	38.07	42.62	³ 9.83
	7	27.61	30.58	314	2.08	6.54	.1906	35.04	41.58	11.00
	¹ 8	29.58	32.54	296	2.28	6.76	.1961	38.62	45.38	12.84
Cowpea.....	13	28.45	31.22	452	2.67	12.05	.1962	37.16	49.21	17.99
	¹ 14	29.08	31.85	436	2.79	12.17	.1939	37.55	49.72	17.87
	15	27.55	30.30	418	2.78	11.63	.1919	35.20	46.83	16.53
	² 16	28.34	31.10	436	2.79	12.13	.1955	36.89	49.07	17.97

¹ Received an extra amount of phosphorus in the manures.

² Received an extra amount of potassium in the manures.

³ The crop was abnormal in 1909, owing to injury from nematodes.

NOTE.—On an area basis, to calculate from the grams per pot to pounds per acre, multiply by 122.4.

REPORT ON INORGANIC PLANT CONSTITUENTS.

By O. M. SHEDD, *Referee*.

The cooperative work on this subject during the present year has consisted in a comparison of two methods for the separation of ferric and aluminic oxides in an ash solution.

The customary letter asking for cooperation was sent to the various stations in January, and favorable replies were received from 21 analysts, who expressed a desire to assist in the work. To them the directions and samples were sent in February, and results have been received from 10, who have completed all or some part of the work as requested.

COMPOSITION OF SAMPLE.

The sample sent out was a synthetic hydrochloric acid solution of an ash and represented an ash having the following composition, the silica, chlorin, and carbon dioxide not being taken into account:

	Per cent.		Per cent.
K ₂ O	40.00	Al ₂ O ₃	2.00
Na ₂ O	3.00	Mn ₂ O ₄	1.00
CaO	23.00	P ₂ O ₅	16.81
MgO	10.00	SO ₃	0.50
Fe ₂ O ₃	3.00		

The iron and aluminum used in this solution were obtained from tested chemically pure iron wire and sheet aluminum. The other chemicals used were chemically pure salts, and a control containing all except the iron and aluminum showed that neither of them was present.

METHODS OF ANALYSIS.

The methods and the results obtained by the different analysts who have cooperated in the work are given below.

MOLYBDATE METHOD FOR FERRIC AND ALUMINIC OXIDS.

Use 50 cc aliquots, corresponding to 0.5 gram of ash, for the determination. If there is ferrous iron present, oxidize by boiling with a few cubic centimeters of hydrogen peroxid. Cool the solution, add ammonium hydroxid until a precipitate begins to form, then nitric acid until just clear, and finally add about 2 to 3 cc of concentrated nitric acid in excess. Add 25 cc of ammonium nitrate solution (1:1) free from phosphate, heat to 40° C., and precipitate the phosphomolybdate by adding slowly, with constant shaking, a moderate excess of the official nitric acid molybdate solution.

The temperature of the solution should not at any time exceed 40° C., as a higher temperature has a tendency to precipitate iron and aluminum with the phosphomolybdate.

After the precipitation is made, allow the solution to stand for an hour or two at 40° C., and then for several hours at room temperature, preferably overnight.

After standing for an hour, make sure that sufficient molybdate solution has been added by pipetting 5 cc of the clear solution into an equal volume of the warm reagent. If a precipitate forms, the test portion is to be returned and more molybdate solution added. Filter and wash with about 75 cc of ammonium nitrate solution (2.5 per cent) slightly acidified with nitric acid and free from phosphate, collecting filtrate and washings.

Do not concentrate the solution, because molybdic acid will separate, which will vitiate the results, but cautiously neutralize it in a beaker with ammonium hydroxid, care being taken that the temperature does not rise above 40° C. and that the alkali is added only in very slight excess; allow to stand at the above temperature until the precipitate completely settles. Filter the clear supernatant fluid, wash the precipitate a couple of times with hot water by decantation before transferring it to the filter, and wash four or five times on the filter. Dissolve the precipitate through the filter with weak, hot nitric acid (1:5), wash the filter, and reprecipitate in the same careful manner. The same filter may be used for the second filtration and the volume of the solution for the reprecipitation need not exceed 100 cc. Before the second filtration is made a small quantity of finely divided ashless filter paper pulp is added in order to facilitate the washing and to leave the precipitate finely divided after the ignition so that it can be easily fused with potassium bisulphate for the iron determination. Dry and ignite the precipitate and weigh as ferric and aluminic oxids.

If the precipitate has been treated as indicated the iron oxid can be readily determined as follows: Fuse it with about 4 grams of potassium bisulphate, cool, add 5 cc of concentrated sulphuric acid, and heat to boiling. Transfer to a flask, add water, and digest until all sulphate is dissolved and the solution is clear. Reduce with zinc, cool, and titrate with a fiftieth-normal solution of potassium permanganate. Make blank determinations on chemicals used.

If it is desired to use a larger amount of the sample for the iron determination a suitable aliquot of the original solution can be taken and evaporated directly with sulphuric acid, reduced with zinc, and titrated as described.

OXALATE METHOD FOR FERRIC AND ALUMINIC OXIDS.

Use 100 cc (1 gram) of the sample and, if the iron has not been already oxidized, add a few cubic centimeters of hydrogen peroxid, boil for a few minutes to oxidize the iron and expel oxygen. Add ammonium hydroxid until a precipitate begins to form, then hydrochloric acid until just clear, then 1.5

grams of powdered ammonium oxalate, boil gently for a short time, shaking occasionally to avoid bumping. Let settle, filter and wash the precipitated calcium oxalate. Collect the filtrate and wash water in a 500 cc Kjeldahl flask, add 5 cc of concentrated sulphuric acid, and evaporate to white fumes to destroy excess of oxalic acid. (This boiling down and destruction of oxalic acid can be done in 20 minutes, and during the first part of the boiling care should be taken to prevent bumping, which can be avoided by adding a few small pieces of scrap platinum.) Cool, add 1 gram of ammonium phosphate, 50 cc of water, and 5 cc of concentrated hydrochloric acid. Boil gently a few moments to dissolve any dehydrated ferric sulphate, boiling until the solution is clear, care being taken that the volume is not appreciably reduced. Rinse into a beaker, make up to about 150 cc volume, and precipitate the iron and alumina as phosphates by adding ammonium hydroxid until just alkaline, just clearing with hydrochloric acid, and then adding 25 cc of ammonium acetate solution (sp. gr. 1.04). Or, if preferred, the solution can be treated as in the Kjeldahl flask and poured in a thin stream into the acetate solution, using sufficient water in the rinsing to bring the total volume to that indicated above. A small amount of finely divided ashless filter paper pulp is added to the phosphates, in order to facilitate the washing and to leave them finely divided after the ignition, so that they can be easily fused with potassium bisulphate for the iron determination.

Have both the ammonium acetate solution and the solution containing the phosphates at 80° C. when the two are combined. Heat the phosphates for 10 minutes at 80° C., filter, using suction, and wash with boiling hot ammonium nitrate solution (2.5 per cent) free from phosphate. Carefully ignite the precipitate without removing from the paper, at first with low flame until the paper is charred, gradually increase the heat until all of the carbon is gone, and finally blast for a minute. Deduct the iron phosphate present, calculated from the iron determination, and multiply the remainder by 0.418 to obtain the alumina.

If the precipitate has been treated as indicated, the iron oxid can be readily determined by fusing it with about 4 grams of potassium bisulphate, cooling, adding 5 cc of concentrated sulphuric acid, and heating to boiling. Transfer to a flask, add water, and digest until all sulphate is dissolved and the solution is clear. Reduce with zinc, cool, and titrate with a fiftieth-normal solution of potassium permanganate. Make blank determinations on chemicals used.

If it is desired to use a larger amount of the sample for the iron determination, a suitable aliquot of the original solution can be evaporated directly with sulphuric acid, reduced with zinc, and titrated as just described.

ANALYTICAL RESULTS.

Separation of ferric and aluminic oxids.

[Synthetic ash solution containing 3 per cent Fe_2O_3 and 2 per cent Al_2O_3 .]

Analyst.	Molybdate method.			Oxalate method.		
	Ferric oxid.	Aluminic oxid.	Ferric and aluminic oxids.	Ferric oxid.	Aluminic oxid.	Ferric and aluminic oxids.
Laboratory, Stillwell & Gladding, New York City..	13.07	12.11	5.15
	13.00	12.15	5.19
	11.99	5.03
	3.04	2.08	5.12
G. E. Boltz, Wooster, Ohio.....	2.98	2.02	5.00	3.02	2.07	5.09
	2.06	5.04	2.98	2.05	5.03
	2.06	5.04	2.98	2.07	5.05
	2.94	2.19	5.13
	2.98	2.05	5.03	2.98	2.10	5.08

¹ These results are not included in the general average for ferric and aluminic oxids, because the ferric oxid was obtained by direct evaporation with sulphuric acid.

Separation of ferric and aluminic oxids—Continued.

Analyst.	Molybdate method.			Oxalate method.		
	Ferric oxid.	Alumi-nic oxid.	Ferric and alumi-nic oxids.	Ferric oxid.	Alumi-nic oxid.	Ferric and alumi-nic oxids.
J. P. Aumer, Urbana, Ill.....	2.71 2.77 2.74 2.62 2.65	2.81 2.43 2.36 2.40 2.71	5.52 5.20 5.10 5.02 5.36	¹ 1.51 ¹ 1.81 ¹ 1.38 ¹ 1.28 ¹ 1.65 ¹ 1.35	10.68 ¹ 1.03 1.49 1.59 1.16 1.31	¹ 2.19 ¹ 2.84 ¹ 1.87 ¹ 1.87 ¹ 1.81 ¹ 1.66
	2.70	2.54	5.24	1.33	.54	1.87
L. T. Bowser, Dayton, Ohio.....	2.86 2.84 2.91 2.92	2.40 2.48 2.53 2.32	5.26 5.32 5.44 5.24	2.90 2.98 2.65 3.10	13.58 16.16 15.24 13.43	16.48 19.14 17.89 16.53
	2.88	2.43	5.31	2.91	4.60	7.51
A. T. Charron, Ottawa, Canada.....	¹ 1.90 ¹ 1.94 ¹ 1.94	¹ 4.82 ¹ 4.98 ¹ 4.74	¹ 6.72 ¹ 6.92 ¹ 6.68	¹ 1.74 ¹ 1.60 ¹ 1.76	13.65 13.73 13.57	5.39 5.33 5.33
	1.93	4.85	6.78	1.70	3.65	5.35
W. L. Hadlock, Pullman, Wash.....	5.72 5.42 5.48 5.36 5.52 5.28
	5.46
P. A. Yoder, Washington, D. C.....	3.31 3.48 3.45 3.19	2.01 2.18 2.12 2.20	5.32 5.66 5.57 5.39	2.85 2.83	2.27 2.12	5.12 4.95
	3.36	2.13	5.49	2.84	2.19	5.03
L. H. Bailey, Washington, D. C.....	3.22 3.12	1.90 2.10	5.12 5.22
	3.17	2.00	5.17
J. F. Breazeale, Washington, D. C.....	5.18
O. M. Shedd, Lexington, Ky.....	3.01 2.95 3.03 2.99 2.97 3.00 3.00 3.12 3.06 3.03 2.92 2.98 2.92 2.95 3.05 3.03 3.00	2.13 2.07 2.31 1.85 2.23 2.18 1.90 2.18 2.22 2.15 2.24 2.16 2.26 2.23 1.93 1.79 2.04	5.14 5.02 5.34 4.84 5.20 5.18 4.90 5.30 5.28 5.18 5.16 5.14 5.18 5.18 4.98 4.82 5.04	2.95 3.01 2.98 3.15 2.82 2.97 3.00 2.93 2.95 2.96 2.97 2.99 2.94 2.97	2.32 2.29 2.27 2.19 2.45 2.34 2.42 2.52 2.41 2.38 2.50 2.47 2.40 2.40	5.27 5.30 5.25 5.34 5.27 5.31 5.42 5.45 5.36 5.34 5.47 5.46 5.34 5.37
	3.00	2.11	5.11	2.97	2.38	5.35
Number of determinations.....	33	35	42	24	20	26
General average.....	2.99	2.20	5.23	2.95	2.31	5.26

¹ Omitted from the general average.

COMMENTS BY ANALYSTS.

Stillwell & Gladding: The ferric oxid was obtained by direct evaporation.

J. P. Aumer: A separate precipitation in the filtrates of the last four of the six determinations, according to the oxalate method, gave the following amounts of ferric and aluminic oxids, respectively: 0.89, 0.74, 0.34, 0.18 per cent; 0.41, 0.38, 0.15, and 0.14 per cent. Further, these second filtrates, upon long standing, still showed phosphate present.

L. T. Bowser: Ferric oxid by direct evaporation with sulphuric acid gave 3.12 per cent and 3.13 per cent.

P. A. Yoder: The following results on ferric oxid were obtained by rereducing the first two solutions of ferric oxid under the molybdate method and retitrating the same. These at first gave 3.31 and 3.48 per cent of ferric oxid. The subsequent retitrations gave 3.13, 3.73, 3.12, and 3.51 per cent of ferric oxid. Retitrations tried on the two solutions under the oxalate method gave 2.88, 2.83, 2.65, and 2.93 per cent of ferric oxid. By direct evaporation of the original ash solution with sulphuric acid, the result obtained was 2.91 per cent of ferric oxid.

L. H. Bailey: Reported that no concordant results could be obtained by the oxalate method.

Note by the referee: Some difficulty seems to have been experienced by a few cooperators in making the iron determination by the bisulphate fusion, undoubtedly due to an incomplete fusion. For this reason, an alternative method for this determination has been added for future work. The last paragraphs of each method for ferric and aluminic oxids, as given in this report, were not included in the methods as sent out for cooperative work, consequently all of the determinations on ferric oxid reported, unless otherwise stated, were made by fusing the precipitate of the double oxids or phosphates with potassium bisulphate.

ADDITIONAL WORK BY THE REFEREES.

In addition, the following results were obtained from W. H. McIntire, of the Pennsylvania State College, who is the associate referee in this work, but they were not received in time to be incorporated in the preceding table. By the molybdate method Mr. McIntire obtained for the sum of the ferric and aluminic oxids: 3.90, 3.90, 3.94, and 4.04 per cent. Average, 3.95 per cent.

Some work has been carried on by the referee on the synthetic solution, extending and applying the molybdate method for the determination of calcium and magnesium in the filtrate from the ammonium hydrate precipitate, disregarding the manganese present. Ordinarily, there will not be as much manganese in an ash as was present in the above solution, and if a determination is desired it can be made separately.

A large amount of work has been done by the referee in perfecting this method, and in the form in which it is now presented excellent results have been obtained by its use. Disregarding the manganese, which does not apparently interfere in an amount as large as that present in the solution, results have been obtained for the calcium and magnesium which agree very closely with the amounts present. As the synthetic solution was prepared chiefly for the iron and aluminium content, small differences in the other bases might be due to impurities, moisture, etc.

It is not the intention of the referee to have the new scheme of analysis take the place of the present one, but rather to supplement it, if after it has been tested by the association it is found satisfactory, as there is no doubt that there will be much time and work saved by using it. The method will have another advantage in that the phosphoric acid, ferric and aluminic oxids, calcium and magnesium oxids, and possibly the manganese can be estimated in

the same solution on one-half gram of ash, which is very desirable when the sample is small. Still another advantage which might be mentioned in its favor consists in avoiding the acetate separation, which at best is not very satisfactory in the hands of the average analyst.

There are some additional points that remain to be settled as to the new procedure, one of which is to see if larger amounts of manganese will interfere, and if such is found to be the case, then a separation of this also may be found to work. No work on the separation of the manganese has been tried by the referee, but the associate referee has done some work along this line and obtained some very promising results (p. 66).

The method found by the referee to give the best results in extending the molybdate method for calcium and magnesium is as follows:

Combine the filtrate and washings from the first and second precipitations of ferric and aluminium hydroxids, make strongly alkaline by adding 5 cc of strong ammonium hydroxid, and heat to 100° C. on the water bath. The volume at this point is probably 400–500 cc. Do not concentrate, but add slowly, with constant stirring, an excess of hot ammonium oxalate solution until the calcium is precipitated. Allow the beaker to remain for a few minutes on the water bath, and after the precipitate settles, filter. The time required for the precipitation is about the same as in an ordinary calcium determination.

Dissolve the calcium oxalate in hydrochloric acid, wash the filter, and add a few drops of ammonium oxalate solution. Then add sufficient water to make a volume of about 75–100 cc, heat to 100° C., and reprecipitate the calcium by adding weak ammonium hydroxid slowly with constant shaking until the solution is faintly alkaline.

Combine the filtrates and washings from both precipitations of the calcium and evaporate to about 100 cc, or to as small a volume as possible, so that the salts will remain in solution on cooling. Make the solution slightly acid with hydrochloric acid, add sufficient sodium phosphate solution to precipitate the magnesium and make the whole slightly alkaline with ammonium hydroxid. Stir or shake the solution until the precipitate forms, and then make strongly alkaline by adding 20 cc of strong ammonium hydroxid. Let stand about 24 hours, filter, dissolve the precipitate in hydrochloric acid and reprecipitate in the same manner as before, keeping the volume as small as possible.

Using this method, the following results on the calcium and magnesium were obtained: Calcium oxid, 23.14, 23.48, 23.10, and 23.12 per cent; magnesium oxid, 9.92 and 9.90 per cent.

In working out the method, a number of determinations of the calcium oxid were made by discarding the filtrate from the reprecipitation of the ferric and aluminum hydroxids and not reprecipitating the calcium oxalate.

The results obtained were: Calcium oxid, 23.10, 23.24, 23.26, 23.12, 22.92, 23.12, and 23.02 per cent. A reprecipitation of the calcium oxalate working in the same manner gave 23.06 per cent of calcium oxid. These determinations were made for the purpose of finding out if it was possible to shorten the method.

While the results given are very good, there has been a balancing of errors to a certain extent in that a small amount of calcium is lost in the filtrate discarded, while more or less manganese is present in the first precipitation of the calcium oxalate. It has been the referee's experience that it is necessary to make reprecipitations in every case in order to obtain pure precipitates, and to save both filtrates and the first washings of all precipitates. Especially is this true if a good determination of the magnesium is desired.

The magnesium determination has given the most trouble in this work and several different plans of precipitating the magnesium ammonium phosphate were tried before the best conditions were obtained. The plan was tried of precipitating in a large volume, 800–1,000 cc, with the ammonium salts present

as prescribed by Washington in his book on rock analyses. Also, the plan was tried of burning off the ammonium salts carefully, taking up the residue with a small amount of acid, and then precipitating the magnesium in a small volume both by leaving the molybdenum in the solution and also by removing most of it by first filtering the oxids of molybdenum while they were in the acid solution and washing the residue. In all cases the results on the magnesium were too low and the only satisfactory plan found was to leave the ammonium salts in the solution and keep the volume as low as possible so that they would remain in solution during the precipitation of the magnesium ammonium phosphate.

Mr. McIntire, the associate referee, by a method but slightly different from the general method already given, has determined the manganese in addition to the calcium and magnesium in the synthetic solution. The method followed was to precipitate the iron and aluminum hydroxids by the directions given and determine the calcium without concentrating the filtrate by means of ammonium hydroxid and ammonium oxalate. After the elimination of the calcium, the filtrates and washings were evaporated to a small volume and the manganese removed by treatment with bromin water. The filtrate from the manganese was evaporated to about 75 cc and precipitated with sodium phosphate. Following this method the following results were obtained:

Determinations, including manganese, by McIntire.

Aluminic and ferric oxids.	Calcium oxid.	Manga- nese (Mn_2O_4).	Magnesi- um oxid.
<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
3.90	24.28	1.16	9.61
3.90	23.88	1.16	9.34
3.94	1.28	9.90
4.04

Mr. McIntire suggests that as most plants contain such a small amount of manganese it would be preferable to leave it in the solution and weigh it with the magnesium as the pyrophosphate. The manganese result could then be obtained by dissolving this precipitate and using the sodium bismuthate method.

The referee's results on magnesium seem to indicate that very little if any manganese in this particular solution is precipitated with the magnesium, but this is a point that needs further investigation.

RECOMMENDATIONS.

Following are the recommendations for the present year—

(1) That the molybdate method in the form in which it is now presented for the separation of ferric and aluminic oxids in an ash solution be made official.

(2) That the oxalate method for the above separations be made a provisional method. That further work be done on it next year on a synthetic solution, in order that it may be made an optional method. This method was first suggested by the referee last year, and in a slightly modified form has been published in the Proceedings for 1910.

(3) That cooperative work be done next year on the molybdate method as extended and described for the separation of calcium and magnesium, and probably the manganese in an ash solution.

(4) That cooperative work be done on the method entitled "The Determination of Total Sulphur in Organic Matter," as described by Herman Schreiber in Circular No. 56, Bureau of Chemistry, United States Department of Agriculture. This recommendation is made in order that there may be an optional official method for the determination of total sulphur in plants, which is very desirable.

The work done in this and former years justifies the first two recommendations. The molybdate method has been before the association since 1903, in which year it was recommended by the referee to be made an official method. Since that time 27 analysts have used it at different times in cooperative work for this association, and with very few exceptions have obtained good results.

The second recommendation is made in order that the association may have another method which will be satisfactory for these separations.

The third needs no further comment, while the fourth recommendation, as stated before, is made simply for the reason that it is very desirable to have a check method for the determination of total sulphur in plants.

In addition, Mr. McIntire, the associate referee, desires the association to take some action upon a recommendation which he set forth in a brief report to the chairman of subcommittee A, as follows:

I would strongly recommend that the method for the preparation of an ash without the use of calcium acetate, which is now an optional official method (Bul. 107, Rev., p. 233), be made the official method for the securing of an ash of different plants, most especially of the cereal plants, because of the fact that there are very minute traces of calcium to be found in these crops, even when grown in the most calcareous soils. In the method calling for the use of calcium acetate, we, of course, are subject to error in the standardization of the chemically pure salt. Afterwards, in making determination of the calcium added to the solution, plus the amount found in the plant, we have a rather large precipitate, a very small percentage of which would make a relatively large error in the actual amount of calcium present in the plant.

The referee is of the opinion that Mr. McIntire's recommendation is a good one in regard to the ashing of a large number of plants, and, furthermore, whatever action is taken by this association, we should, as far as possible, describe the kind of plants to which each method of ashing is best suited.

Three resolutions offered by Mr. Shedd, amending the constitution and by-laws, were referred to Mr. Van Slyke as chairman of the committee on amendments to the constitution (see p. 86).

At 1.40 the convention adjourned until 2 p. m.

MONDAY—AFTERNOON SESSION.

At the opening of the afternoon session the president appointed the following committees:

Committee to invite the Secretary of Agriculture and the Assistant Secretary to address the association: M. E. Jaffa, of California; F. T. Shutt, of Canada; and A. J. Patten, of Michigan.

Committee on resolutions: William Frear, of Pennsylvania; B. B. Ross, of Alabama; and J. G. Lipman, of New Jersey.

Committee on nominations: L. L. Van Slyke, of New York; W. A. Withers, of North Carolina; and B. L. Hartwell, of Rhode Island.

Auditing committee: J. M. Bartlett, of Maine; O. M. Shedd, of Kentucky; and C. W. Stoddart, of Pennsylvania. (B. L. Hartwell, Rhode Island, acting in the absence of Mr. Stoddart.)

REPORT ON INSECTICIDES.

By C. C. McDONNELL, *Referee.*

The cooperative work on the subject of insecticides and fungicides this year has consisted of work on methods for the analysis of lead arsenate and lime-sulphur solutions. Reports have been received from five laboratories in addition to the work done in the Insecticide Laboratory of the Bureau of Chemistry.

LEAD ARSENATE.

The work on this material has been carried out along the lines recommended by the referee and adopted by the association last year. Two samples were submitted for analysis, No. 1 being a commercial sample of lead arsenate paste, and No. 2 a sample prepared in the laboratory from pure chemicals. The determinations of moisture, total lead oxid, and water-soluble arsenic by the following methods were requested:

Moisture.—In case the sample is in the form of a paste (sample No. 1), weigh entire sample and dry at from 80° to 100° C. until dry enough to powder readily, and obtain loss in weight. Powder the dried sample in a mortar and determine the remaining moisture as follows: Dry 2 grams in an air oven at 105° to 110° C. to constant weight. Calculate total moisture from this loss and the loss obtained in the preliminary drying.

On sample No. 2 obtain moisture by drying 2 grams to constant weight at 105° to 110° C.

Lead oxid.—*Method I.*—See Bureau of Chemistry Bulletin 107, Revised, page 239.

Method II.—Treat 2 grams of the powdered sample with 50 cc of nitric acid (1:4), heat the solution, and when the lead arsenate has dissolved, cool, and make up to 200 cc. Pipette 50 cc of this solution into a 400 cc beaker, dilute to about 300 cc, heat nearly to boiling, add sodium or ammonium hydroxid to incipient precipitation, then add dilute nitric acid (1:10) to redissolve the precipitate, avoiding more than a slight excess; now add to this boiling solution 50 cc of a 10 per cent potassium chromate solution, stirring vigorously during the addition. The chromate solution should be nearly boiling and added to the lead solution by means of a pipette delivering 50 cc in about one minute. If the lead chromate is precipitated hot and stirred vigorously during the precipitation it will settle clear in 15 minutes, or less, when it is ready to be filtered. Filter while hot, collecting the precipitate on a weighed gooch, and wash with boiling distilled water until the final wash water does not show the slightest tinge of yellow. Dry the precipitate in an air oven at 140° to 150° C. to constant weight. (In preparing the filter, the asbestos mat should be thick and pressed down firmly, then washed, and dried at 140° to 150° to constant weight. If porcelain gooch crucibles are used they should be cooled in a desiccator over sulphuric acid, as they take up a little moisture over calcium chlorid.)

Weight of $\text{PbCrO}_4 \times 0.6905 = \text{PbO}$.

Soluble arsenic.—(1) Method as given in Bureau of Chemistry Bulletin 107, Revised, page 240. Use 500 cc of the water extract for the determination of arsenic. Make correction for the amount of iodine solution required to produce blue color titrated to—using same chemicals and volume as in the determination.

(2) Determine water-soluble arsenic as before, except digest for one day instead of ten.

The results reported by the various analysts are given in the following table:

Cooperative results on lead arsenate.

[Results on lead and arsenic oxids calculated to "moisture-free" basis.]

Analyst.	Sample No. 1.						Sample No. 2.					
	Mois- ture.	Total lead oxid (PbO).		Water-solu- ble arsenic oxid (As ₂ O ₅).		Mois- ture.	Total lead oxid (PbO).		Water-solu- ble arsenic oxid (As ₂ O ₅).			
		Meth- od I.	Meth- od II.	Extraction.			Meth- od I.	Meth- od II.	Extraction.			
				10 days.	1 day.				10 days.	1 day.		
S. D. Averitt, Lexington, Ky.	<i>P. ct.</i> 40.30	<i>P. ct.</i> 69.17	<i>P. ct.</i> 69.72	<i>P. ct.</i> 1.09	<i>P. ct.</i> 0.85	<i>P. ct.</i> 4.15	<i>P. ct.</i> 62.52	<i>P. ct.</i> 62.67	<i>P. ct.</i> 0.25	<i>P. ct.</i> 0.25		
R. J. Davidson and C. B. Walker, Blacksburg, Va.	39.84	69.30	69.55	1.11	.87	62.40	62.65	.28	.25			
	69.40	69.55	70.13	.99	.60	4.09	61.30	62.75	.20	.12		
	69.40	70.11	.94	.60		61.41	62.77	.22	.12			
	69.40	70.06				61.18						
C. H. Robinson, Ottawa, Canada ...	39.32	69.11	69.45	.78	.59	4.18	62.09	62.84	.14	.12		
	69.11	69.37	.78	.59		62.09	62.67	.14	.12			
	69.10	68.65	.68	.51		62.14	62.55	.14	.11			
A. T. Charron, Ottawa, Canada	69.04	68.65	.70	.51		62.04	62.54	.14	.11			
		68.56					62.56					
Miss M. E. Stover, Berkeley, Cal... L. T. Bowser, Dayton, Ohio.	39.26 40.04	69.46 69.12	68.87	.31	.23	4.24	62.01	62.54	.13	.03		
		69.22	69.44	1.10	.61	4.13	62.45	62.38	.33	.09		
		69.44	69.46	.96	.67	4.06	62.41	62.43	.33	.06		
		69.34	69.62	.99	.61		62.48	62.63		.06		
			69.59				62.50	62.47				
W. D. Lynch, Washington, D. C. ...	39.72	69.65	69.44	.70	.48	4.17	62.77	62.88	.07	.03		
	69.49	69.53	.70	.48		62.90	62.82	.06	.03			
R. C. Roark, Washington, D. C. ...	39.51	69.43	69.69	.81	.68	3.97	62.19	62.91	.09	.05		
	69.29	69.62				62.30	62.95					
	69.16	69.41					62.83					
C. C. McDonnell, Washington, D. C.	40.07	69.38	69.70	.70	.60	4.13	62.44	62.89	.08	.06		
		69.65	69.75	.70	.60		62.54	62.88	.08	.06		
Average.....	39.76	69.32	69.47	.83	.59	4.12	62.21	62.70	.17	.10		

Mr. Averitt, the associate referee, reports Method II for total lead as "easy to work, rapid, and accurate." For soluble arsenic he suggests shaking every quarter hour during a working day and filtering after standing overnight. Mr. Bowser reports "the chromate method seems very good, and I am making use of it on other work to advantage." He suggests that acid and alkali of known strength be used in preparing the solution in order to avoid getting too large an excess of nitric acid before precipitating with the chromate solution.

The results on total lead oxid by the sulphate method agree well. Neither of the samples contains calcium salts, which would render this method unreliable. The results by the chromate method do not agree quite so well, but in consideration of the fact that it is the first time it has been submitted for trial they can be considered quite satisfactory. The point about the method which demands care is to avoid leaving more than a slight excess of nitric acid when making the precipitation. By using dilute acid and adding it carefully there need be no trouble from this cause. It has been found in this laboratory that ammonium hydroxid is a little more desirable for neutralizing excess acid than sodium hydroxid; the lead chromate precipitate collects better, and slightly more satisfactory results are obtained. This method has been in use in this laboratory for the past two years and has always given satisfactory results. I have no hesitancy in recommending its adoption as an official method.

The results on water-soluble arsenic are not entirely satisfactory. In the carrying out of the method there are several points which must be observed. In the first place, in filtering the solution after digesting the lead arsenate with water certain samples have a tendency to run through the filter, and in some cases it is almost impossible to obtain a clear filtrate. We have found that by

shaking up the sample just before filtering a clear filtrate can usually be obtained after discarding the first portion that comes through. The temperature of the water during the digestion has a slight influence on the amount dissolved. Great care must be exercised in the addition of thiosulphate and in the final titration with iodine. Where the amount of arsenic present is so small, an error of a drop or two of either of these solutions will make a marked difference in the results. In view of the determinations reported and awaiting the results of other work which we are now doing relative to time of digestion, temperature, etc., no recommendation will be made at this time.

The results on moisture show a satisfactory agreement.

LIME-SULPHUR SOLUTIONS.

On account of the necessity of having official methods for the determination of the various sulphur compounds in lime-sulphur solutions, those here given were submitted for trial. They are, with slight modifications, the same as given in Bureau of Chemistry Bulletin 101, page 9, which have been adapted from methods given in Sutton's Volumetric Analysis, and Avery's method for total sulphur as adopted by the association in 1909:

Total sulphur in solution.—Bureau of Chemistry Bulletin 107, Revised, page 34. Instead of measuring 10 cc of the sample, weigh accurately about 10 grams and make up to 100 cc. Use 10 cc aliquots of this for each determination.

Sulphur as sulphids.—Dilute 10 cc of the solution, prepared as for total sulphur, to about 100 cc and add ammoniacal zinc chlorid solution (prepared by dissolving 50 grams pure zinc chlorid in water and adding ammonia in sufficient quantity to redissolve the precipitation first formed) until the sulphid is all precipitated, as will be shown by adding a drop of the clear solution to a few drops of nickel sulphate solution. Place on steam bath and heat until the odor of ammonia becomes faint, then filter and wash the precipitate. Transfer filter containing the zinc sulphid precipitate to a beaker, add 10 to 15 cc of a saturated solution of sodium or potassium hydroxid and heat on steam bath for about 15 minutes. Dilute with about an equal quantity of water, add 50 cc hydrogen peroxid solution, and heat on steam bath for 30 minutes. Then make the solution slightly acid with hydrochloric acid, filter to remove paper, wash thoroughly, heat to boiling, and precipitate the sulphate with barium chlorid solution. Calculate sulphid sulphur from the weight of barium sulphate obtained.

(Make blank determinations of sulphur (SO_2) in the reagents used in the determinations of total and sulphid sulphur and make correction therefor. If the hydrogen peroxid solution is not full strength, 50 cc may not be sufficient to oxidize all the sulphur compounds to sulphate, in which case more peroxid must be used.)

Sulphur as thiosulphate.—Dilute 20 cc of the solution prepared as for total sulphur to about 50 cc in a 200 cc graduated flask. Add ammoniacal zinc chlorid until in slight excess and make to mark. Shake thoroughly and filter through a dry filter. To 100 cc of the filtrate add methyl orange and exactly neutralize with dilute hydrochloric acid. Titrate this solution with tenth-normal iodine, using a few drops of starch paste as indicator. From the amount of iodine solution required calculate the sulphur present as thiosulphate, as represented by the following reaction: $2\text{Na}_2\text{S}_2\text{O}_3 + 2\text{I} = 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6$.

Sulphur as sulphate and sulphite.—To the solution from the determination of thiosulphate add two or three drops of hydrochloric acid, heat to boiling, precipitate with barium chlorid solution, and obtain weight of barium sulphate, from which calculate sulphur and report as "sulphate and sulphite sulphur."

Note.—In case sulphite is present the determination of thiosulphate will be too high. However, as calcium sulphite is nearly insoluble it will not be present in more than traces, and the error from this cause will be negligible. We have never examined a sample of lime sulphur in which the combined sulphate and sulphite amounted to more than a small fraction of a per cent.

Two samples were submitted for the work, which were prepared as follows: Weighed amounts of lime, sulphur, and water were boiled together, and two measured portions of the clear solution thus obtained were used. No. 1 was

diluted to a definite volume with water and No. 2 was diluted to the same volume with a solution containing a weighed amount of sodium thiosulphate, from which, by calculation, sample No. 2 contained 2.02 per cent of sulphur as thiosulphate in excess of that in No. 1. Owing to the difference in the specific gravity of the two solutions the sulphid sulphur in No. 2 should be 0.4 per cent lower than in No. 1, assuming that no chemical change has taken place in the samples.

Cooperative results on lime-sulphur.

Analyst.	Sample No. 1.				Sample No. 2.			
	Total sulphur.	Sulphid sulphur.	Thio-sulphate sulphur.	Sulphate sulphur.	Total sulphur.	Sulphid sulphur.	Thio-sulphate sulphur.	Sulphate sulphur.
R. Davidson and C. B. Walker, Blacksburg, Va.....	P. ct. 12.48 12.49 12.49 12.46	P. ct. 10.78 10.78 10.80	P. ct. 1.85 1.85 1.85	P. ct.	P. ct. 14.84 14.86 14.33	P. ct. 10.12 10.18 10.33	P. ct. 3.82 3.82 3.82	P. ct.
S. D. Averitt Lexington, Ky.....	12.28 12.23 12.28	10.19 10.33	1.80 1.87 1.81	0.03 .02 .04	13.75 13.82 13.74	10.32 10.50	3.75 3.83 3.79	0.03 .02 .04
A. T. Charron, Ottawa, Canada.....	12.50 12.49 12.47	10.33 10.32	1.84 1.84	.09 .09	14.12 14.06 14.14	9.85 9.86	3.80 3.80	.24 .26
C. H. Robinson, Ottawa, Canada.....	12.51 12.44	10.39 10.36	1.84 1.84	14.14 14.06	9.83 9.84	3.77 3.77
M. E. Stover, Berkeley, Cal.....	12.45	10.47	1.91	.04	14.13	9.96	4.09	.08
R. C. Roark, Washington, D. C.....	12.22	10.50	1.80	.16	14.02	10.26	3.73	.12
W. D. Lynch, Washington, D. C.....	12.51 12.48 12.45	10.57 10.48 10.42	1.80 1.80 1.82	.13 .04 .06	14.07 14.07 14.11	10.44 10.36 10.34	3.63 3.84 3.82	.12 .06 .08
C. C. McDonnell, Washington, D. C..	12.14 12.15	10.40 10.32	1.83 1.84	.02 .03	14.11 10.10	10.11 3.92	3.81 3.92	.05 .06
Average.....	12.40	10.40	1.83	.06	14.02	10.16	3.81	.10

¹ Not included in average; no blank run on reagents used.

The results on the lime-sulphur samples are good, as a whole. The thiosulphate determinations are very close and the work shows the method to be accurate. Practically the theoretical amount added to No. 2 is accounted for.

In the determination of sulphate, the solution must not be boiled, because by so doing some sulphate will be formed from decomposition of the tetrathionate, particularly if more than a trace of hydrochloric acid is present and the solution contains a considerable amount of tetrathionate, as in sample No. 2.

In making the precipitation, warm the solution on a steam bath, then add the barium chlorid, stirring the solution well for several minutes, and let stand in the cold overnight before filtering.

RECOMMENDATIONS.

It is recommended—

(1) That the chromate method (Method II) for total lead oxid in lead arsenate be adopted as official.

(2) That the method for water-soluble arsenic oxid in lead arsenate be further studied as regards time of standing for the solution of soluble arsenic and the effect of different temperatures thereon.

(3) That the method for total sulphur in lime-sulphur solutions (Bureau of Chemistry Bul. 107, Rev., p. 34) be changed as follows: Under "2," line 1, after "Measure," insert "and accurately weigh;" after "sample" strike out "in" and insert a comma and the words "transfer to," and the method as thus changed be adopted as official. (By both measuring and weighing the

sample operated upon, the "per cent by weight" and "grams per 100 cc" of the determined constituents can readily be calculated.)

(4) That the gravimetric method for sulphur as sulphids and polysulphids in lime-sulphur solutions, as given in this report, be adopted as official.

(5) That the volumetric method for sulphur occurring as thiosulphate in lime-sulphur solutions, as given in this report, be adopted as official.

(6) That the method here given for sulphur occurring as sulphates and sulphites in lime-sulphur solutions be changed as follows: Strike out "heat to boiling, etc." to end of paragraph, and substitute "warm on steam bath, precipitate with barium chlorid solution, stirring vigorously for several minutes, let stand in the cold overnight, filter and obtain weight of barium sulphate. From this weight calculate sulphur," and that the method as changed be adopted as official.

The following recommendations which were adopted by the association in 1909 are hereby renewed for final action.

(7) That "Method II" for total arsenious oxid in London purple, as given in Bulletin 107, Revised, page 29, be dropped from the methods of analysis.

(8) That "Method II" for total arsenic oxid in London purple, as given in Bulletin 107, Revised, page 29, be dropped from the methods of analysis.

The following recommendations adopted by the association in 1910 are hereby renewed for final action:

(9) That "Method I" for total arsenious oxid in London purple, as given in Bulletin 107, Revised, page 28, be adopted as official.

(10) That "Method III" as proposed by the referee in 1909 (Bul. 132, p. 43) for the total arsenic oxid in London purple be adopted as official and designated as "Method II."

(11) That the Gatehouse method (Sutton's Volumetric Analysis, 9th ed., p. 201; Bureau of Chemistry Cir. 10, Rev., p. 6) for the determination of chlorin in cyanids be adopted as official.

(12) That the provisional methods for the analysis of lead arsenate (Bul. 107, Rev., p. 239) be changed in accordance with recommendation 7 of the referee in 1910 (Bul. 137, p. 47), and as changed be adopted as official. (The additions and changes as recommended were adopted as provisional in 1910.)

The secretary-treasurer of the association presented his report, which was referred to the auditing committee (see p. 212). He also presented the formal invitation of the officers and members of the executive committee of the Eighth International Congress of Applied Chemistry to the association to join the congress and take part in the proceedings, the opening meeting to be held in Washington, September 4, and the subsequent meetings in New York, closing on September 13. Reply to be addressed to Bernhard C. Hesse, 25 Broad Street, New York.

A resolution by Mr. Withers in regard to the appointment of referees by the outgoing executive committee was referred to the committee on amendments to the constitution (see p. 86).

REPORT ON WATER.

By W. W. SKINNER, *Referee*.

The cooperative work on water analysis for this year has been a continuation of the plan of work prosecuted the year previous with a very slight modification in the several methods used. The work, as heretofore, has been restricted

to a consideration of the more common determinations in mineral water analysis, strontium being the only determination which has been added to the work, while lithium has been omitted because of the excellent results of last year obtained by the Gooch method, and partly because to have included it in this year's determinations would probably have made the cooperative work on water rather tediously long. A general letter of invitation to participate in the work was sent to numerous chemists known to be interested in water analysis, 16 of whom responded with a request that samples and directions for the work be forwarded. Ten chemists have submitted results in time to have them incorporated in the report. It was found to be practically impossible to obtain a natural water which would contain the several constituents in sufficient amounts to give a thorough test of the several methods proposed for their determination. It seemed desirable on account of the size of the sample also to have the concentration such that not in excess of 1 liter should be taken for any one determination. With these points in mind, a sample of water was prepared, the basis of which was filtered Potomac River water to which were added known quantities of several salts in which the natural water for our purposes was deemed lacking. The sample after being prepared was allowed to remain in the laboratory for several days with occasional agitation. It was then transferred to the several packages and immediately sent by express to the collaborators, with instructions that the determinations of bicarbonic acid, nitric acid, and chlorin be made as soon after the sample was received as possible, and then if it were necessary to delay the work, that the several portions should be withdrawn for the determinations and acidified with hydrochloric acid in order to prevent any possible action of the water upon the glass container. The following table gives the results obtained by the several analysts. In order to avoid the introduction of any personal element into the report, the names of the analysts have been omitted.

Analysis No. 1 was made in the water laboratory of the Bureau of Chemistry immediately after the sample was prepared and at about the time it was supposed that other analysts would be engaged in the cooperative work.

Analysis No. 2 was made in the water laboratory after the sample had stood in the glass container for six months. It was made by another chemist working independently, who was unaware of the results of analysis No. 1. A comparison of these two analyses shows that the nitric acid, aluminum, and silica are slightly greater in analysis No. 2 where the water had been allowed to stand in the container for a period of six months. The other figures are in reasonably close agreement.

A comparison of the results given in the table for sulphuric acid shows, with one exception, a reasonably close agreement. This exception is in the case of analysis No. 8. It should be noted further, however, that the results submitted by No. 8 are generally incorrect and have been largely omitted from the general average. The agreement would seem to indicate that the technique employed in the determination of sulphates is correct. When, however, sulphates are high, accompanied by a high content of sodium, the results for sulphates are generally too low. This error in the determination of sulphates was pointed out by Allen and Johnston,¹ and by Johnston and Adams², and it is advisable for waters high in these salts to modify the method as suggested by the latter.

The results for bicarbonic acid vary to a considerable extent, but with one exception are within what might be considered a reasonable agreement. The variation in this determination is probably due to the difficulty in reading the end point with methyl orange. It has been our experience that this color change probably causes greater difficulty and uncertainty than any other determination. Part of the difficulty may possibly be attributed to inferior

¹ J. Amer. Chem. Soc., 1910, 32: 588.

² J. Amer. Chem. Soc., 1911, 33: 829.

methyl orange used, as in our laboratory we have had to reject numerous samples of methyl orange before obtaining a supply reasonably sensitive in its reaction.

The results for the determination of nitric acid are very unsatisfactory. It will be noticed that in the two analyses made in this bureau, No. 2 some six months after No. 1, the nitric acid had increased over one part per million. This increase was probably due to the nitrification of the small amount of organic matter contained in the Potomac River water. The results, however, obtained by analysts 4, 5, and 7 are entirely unexplainable. The variation in this determination seems to be a very serious consideration when it is remembered that in a sanitary analysis the judgment of the character of a water supply is often dependent upon the report on the content of nitrate. It is possible that some of the difficulty may be attributed to the use of potassium hydroxid as a neutralizing agent in the place of ammonium hydroxid, as suggested by Chamot. If with this modification the silver salt is not entirely removed in the reaction, incorrect results are apt to occur. For this reason the referee is of the opinion that where the use of ammonium hydroxid is not a serious objection to general laboratory work nothing is to be gained by the substitution of potassium hydroxid for ammonium hydroxid in this determination.

For such a fundamental determination as chlorin a very close agreement would be expected. That such, however, is not the case seems to the referee to be a reflection rather upon the worker than upon the method. The actual chlorin in the sample of water is known to be between 62 and 63 parts per million, and that one analyst should obtain a determination of 73.5 parts and one other a determination of 69, and two others determinations of 67.5 and 67.4, respectively, seems rather astonishing. Using a standard solution of silver nitrate, 1 cc equivalent to 1 mg of chlorin, the 10 parts per million in excess obtained by No. 8 is equivalent to a difference of 1 cc in the titration on 100 cc of water, when the total titration consumed only between 6 and 7 cc. If a weaker solution of silver nitrate is used, i. e., 1 cc equivalent to 0.5 mg chlorin, the difference in the titration is equivalent to 2 cc. In view of the fact that this weaker solution can be read within 0.2 or 0.3 cc with accuracy, this variation would seem to point to a lack of care in preparing the standard solution.

The figures for iron and aluminum are not of very great significance and are approximately in agreement with the amount of these elements known to exist in Potomac River water. The slight increase shown in analysis No. 2 over that of No. 1 is possibly to be explained by contamination from the glass container, possibly silica.

The determinations of calcium are, with the exception of analyses Nos. 6, 8, and 9, fairly satisfactory. It should be noted, however, that No. 9 reports no strontium, while it is known that 3.5 parts per million are present; if the strontium is deducted from the report on calcium it would bring the results in fairly close agreement with the average. The determinations reported in analysis No. 8 are high, but as the strontium is low, it is evident that the calcium figure is contaminated with strontium. However, if the known amount of strontium were subtracted, the result for calcium would still be high. Analysis No. 6 shows 41.2 parts of calcium, but no strontium. Deducting the 3.5 of strontium known to be present from the 41.2 of calcium reported makes the result quite low.

The results on strontium are unsatisfactory and are to be attributed, possibly, to a lack of experience in this determination. The water was known to contain exactly 3.5 parts per million of strontium. It will be noted that of the eight analyses reporting the determination of strontium four had to be omitted from the average because of the wide variation. The method for strontium is as follows:

Dissolve the above oxids (calcium and strontium) with dilute nitric acid and test with the spectroscope for strontium. If strontium is found transfer the nitric acid solution to a small Erlenmeyer flask and evaporate to complete dryness on the steam bath. Heat at 150° to 160° for one or two hours until perfectly dry. Cool, add from 3 to 5 cc of a mixture of equal parts of absolute alcohol and ether. Cork the flask and allow to stand for 12 hours, with occasional shaking. Filter, wash with alcohol ether mixture until a few drops of the filtrate evaporated on platinum foil or watch glass leaves no residue. Evaporate the filtrate to dryness. Dissolve the calcium nitrate in water, precipitate as oxalate, filter, wash, ignite, and weigh as calcium oxid.

Dry the paper and precipitate. Dissolve the strontium nitrate with a few cubic centimeters of hot water. Add a few drops of sulphuric acid, then a volume of alcohol equal to the volume of the solution. Allow to stand 12 hours. Filter, ignite, and weigh as strontium sulphate. Test spectroscopically for absence of calcium.

This method has been very carefully studied in the water laboratory of the Bureau of Chemistry; it has, with proper care, given most excellent results, and is considered much superior to the older ammonium sulphate method originally proposed.

The results for magnesium are fairly satisfactory, with the exception of the figures reported in analyses Nos. 4 and 5. These results are entirely too low and have been omitted from the average.

The data on potassium are satisfactory, with the exception of the results reported by analyst No. 8. In view of the peculiar coincidence in the arrangement of the figures in the report of analyst No. 8, he was communicated with to determine if a typographical error had been made. In reply he stated that the results as reported were obtained. No explanation can be offered for a result of this character.

The figures on sodium are satisfactory, while those for silica show slight variations which may be attributed in some cases to the action of the water upon the container. Thus the increase from 5.2 to 7.9 between analyses Nos. 1 and 2, where it was known that the water had remained in the glass container for a period of six months, indicates a decided solvent action of the water upon the glass.

Results of cooperative work on water.

[Ions in parts per million.]

Determination.	Analyst.							
	No. 1.		No. 2.		No. 3.		No. 4.	
	Ions.	Milligram equivalent.	Ions.	Milligram equivalent.	Ions.	Milligram equivalent.	Ions.	Milligram equivalent.
Sulphuric acid (SO_4).....	72.0	-1.499	72.1	-1.501	73.25	-1.525	71.8	-1.495
Bicarbonic acid (HCO_3).....	173.3	-2.841	181.4	-2.973	178.42	-2.924	201.6	-3.304
Nitric acid (NO_3).....	3.2	-.052	4.4	-.071	4.54	-.073	11.25	-.181
Chlorin (Cl).....	62.0	-1.748	62.5	-1.762	62.75	-1.770	65.2	-1.839
Iron (Fe).....	.2	+.011	.4	+.021	.50	+.027	1.0	+.054
Aluminum (Al).....	.5		1.7				.0	
Calcium (Ca).....	40.8	+2.035	40.3	+2.010	42.24	+2.107	39.4	+1.966
Strontium (Sr).....	3.4	+.078	3.1	+.071	2.51	+.057	1.9	+.043
Magnesium (Mg).....	19.3	+1.587	19.2	+1.579	19.80	+1.628	13.19	+1.085
Potassium (K).....	12.4	+.317	12.9	+.330	12.79	+.327	13.26	+.339
Sodium (Na).....	52.4	+2.278	51.6	+2.243	54.47	+2.368	49.45	+2.150
Silica (SiO_2).....	5.2		7.9		4.32		4.0	
Total.....	444.7		457.5		455.59		472.05	
Sum of plus milligram equivalents.....		+6.306		+6.254		+6.514		+5.695
Sum of minus milligram equivalents.....		-6.140		-6.307		-6.292		-6.819
Difference.....		+.166		-.053		+.222		-1.124

¹ Omitted from average.

Results of cooperative work on water—Continued.

Determination.	Analyst.							
	No. 5.		No. 6.		No. 7.		No. 8.	
	Ions.	Milligram equivalent.	Ions.	Milligram equivalent.	Ions.	Milligram equivalent.	Ions.	Milligram equivalent.
Sulphuric acid (SO ₄).....	72.8	-1.516	72.00	-1.499	73.0	-1.520	177.46	-1.612
Bicarbonic acid (HCO ₃).....	176.9	-2.900	175.56	-2.878	178.4	-2.924	173.85	-2.850
Nitric acid (NO ₃).....	¹ 1.4	-.022	3.18	-.051	¹ 1.29	-.005	4.25	-.068
Chlorin (Cl).....	67.5	-1.904	62.50	-1.762	67.4	-1.901	¹ 73.50	-2.073
Iron (Fe).....	.33	+ .018	.40	+ .021	.91	+ .049	.65	+ .035
Aluminum (Al).....	.86						.35	
Calcium (Ca).....	40.6	+2.025	¹ 41.22	+2.056	37.3	+1.861	¹ 46.53	+2.321
Strontium (Sr).....	¹ 1.6	+ .036	.00	+ .000	¹ 5.3	+ .121	¹ 1.67	+ .038
Magnesium (Mg).....	¹ 14.9	+1.225	18.95	+1.558	18.3	+1.505	17.15	+1.410
Potassium (K).....	11.7	+ .299	13.65	+ .349	12.4	+ .317	¹ 21.97	+ .562
Sodium (Na).....	54.1	+2.352	51.45	+2.237	54.1	+2.352	48.61	+2.113
Silica (SiO ₂).....	4.8		6.85		5.7		7.33	
Total.....	447.49		445.76		453.10		473.32	
Sum of plus milligram equivalents.....		+5.955		+6.221		+6.205		+6.479
Sum of minus milligram equivalents.....		-6.342		-6.190		-6.350		-6.603
Difference.....		-.387		+ .031		-.145		-.124

Determination.	Analyst.				Extremes and means.		
	No. 9.		No. 10.		Highest.	Lowest.	Average.
	Ions.	Milligram equivalent.	Ions.	Milligram equivalent.			
Sulphuric acid (SO ₄).....	72.9	-1.518	71.61	-1.491	73.25	71.61	72.4
Bicarbonic acid (HCO ₃).....	¹ 188.4	-3.088	176.90	-2.900	184.5	173.3	178.9
Nitric acid (NO ₃).....			4.37	-.070	4.54	3.18	3.9
Chlorin (Cl).....	63.93	-1.803	69.15	-1.950	69.15	62.0	65.6
Iron (Fe).....	.22	+ .012	.66	+ .035		.4	1.2
Aluminum (Al).....	.59				2.1		
Calcium (Ca).....	¹ 45.10	+2.251	41.09	+2.050	42.24	37.3	39.8
Strontium (Sr).....			2.95	+ .067	3.4	2.51	3.0
Magnesium (Mg).....	17.84	+1.467	19.33	+1.599	19.8	17.15	18.5
Potassium (K).....	12.86	+ .329	11.27	+ .288	13.65	11.27	12.5
Sodium (Na).....	50.93	+2.216	52.70	+2.291	54.47	48.61	51.5
Silica (SiO ₂).....	3.8		4.80		7.9	3.8	5.8
Total.....	456.62		454.83		475.0	431.13	453.1
Sum of plus milligram equivalents.....		+6.275		+6.321			
Sum of minus milligram equivalents.....		-6.409		-6.411			
Difference.....		-.134		-.090			

¹ Omitted from average.

In order to show the balance of each analysis and bring out more clearly the variations in the comparison, there has been included in the table the milligram-equivalent of each determination with its proper sign. If the analysis is properly balanced, that is, if the basic and acid elements are in proper proportion, the difference between the plus and minus equivalents should be small. The obtaining of this balance in equivalents is a useful method when properly employed for detecting possible errors in a complete mineral analysis.

It also gives more clearly a thorough appreciation of the error of the analysis. Thus, by referring to the chart, it will be noticed that the errors in analyses

Nos. 1 and 2 were $+0.166$ and -0.053 , respectively. This indicates that the algebraic sum of the errors in analysis No. 1 is equivalent to approximately 1.35 per cent, and the sum of the errors in analysis 2 is equivalent to an error of approximately 0.41 per cent. Such balances are to be considered very satisfactory in water of a mineralization similar to this. An inspection of the chart will show that analysis No. 4 is seriously out of balance and should, therefore, be entirely rejected from consideration. In the statement of the general averages and also of the maximum and minimum figures, however, the results of No. 4 have been omitted only where they are shown to be very wide in their variation from the other determinations. While a large plus or minus difference in the algebraic sum of the equivalents indicates that there is a serious error in the analysis, a slight difference does not, on the contrary, always indicate that the analysis is correct, because it is entirely possible for the errors to occur in such manner as to compensate for each other. Thus, in analysis No. 8, in which 5 of the 12 determinations had to be omitted from the general average because of the wide variation, it is noted that the difference is only -0.085 in the balance of the equivalents.

The results of the cooperative work this year, as a whole, are decidedly an improvement over those obtained last year. While numerous results, and in two instances almost the entire analysis, had to be omitted from consideration, the reports are fairly satisfactory and indicate that experience with the methods is all that is necessary to obtain accurate results. While collaborative work is to some extent a test of the men doing it, the primary object, of course, is to arrive at a correct estimate of a proposed method. It is of the highest importance, therefore, that the work submitted has received that painstaking care which its importance warrants.

RECOMMENDATIONS.

It is respectfully recommended that the methods for water analysis proposed in Circular 52 be adopted as provisional methods of the association.

[The following modifications of these methods as printed in Circular 52 are offered for adoption in 1912.]

MODIFIED METHODS FOR THE ANALYSIS OF MINERAL WATERS.

1. TOTAL SALTS IN SOLUTION.

[As in Circular 52, page 6.]

2. LOSS ON IGNITION.

[As in Circular 52, page 6.]

3. SILICA, IRON, ALUMINUM, MANGANESE, CALCIUM, STRONTIUM, MAGNESIUM.

A preliminary examination should be made using from 100 to 250 cc of water to determine the quantity of calcium and magnesium present, which determines the quantity of water to be evaporated for the final analysis.

(a) *Silica.*

Evaporate such quantity of the water that the weight of calcium oxid will be from 0.1 to 0.6 gram or the weight of magnesium pyrophosphate 0.1 to 1.0 gram. Acidify the quantity of water (usually from 1 to 5 liters) with hydrochloric acid and evaporate to dryness in a platinum dish; continue the drying on the water bath for about 1 hour. Drench the residue with hydro-

chloric acid (usually 5 to 15 cc are sufficient). Allow to stand 10 to 15 minutes and add sufficient water to bring the salts into solution. Heat on the steam bath until solution of the salt is effected. Filter and wash thoroughly with hot water. This removes most of the silica. Evaporate the filtrate to dryness; take up with 5 or 10 cc of hydrochloric acid and sufficient water as before. Heat, filter, and wash thoroughly with hot water. The filtrate is solution A. Transfer the two residues to a platinum crucible, ignite, blast, and weigh. Moisten the contents of the crucible with a few drops of water; add a few drops of sulphuric acid and a few cubic centimeters of hydrofluoric acid and evaporate on the water bath under a good hood. Repeat the treatment if all silica is not volatilized. Dry carefully on a hot plate, ignite, blast, and weigh. The difference is silica. The residue in the crucible, usually alumina and iron oxid, is added to the total iron and aluminum oxids later in the analysis.

(b) *Iron and aluminum.*

Concentrate solution A to about 200 cc; while still hot add ammonium hydroxid slowly with constant stirring until it can be faintly smelled coming off from the solution. Boil the solution until the smell of ammonia has nearly but not quite disappeared. Filter and wash two or three times with hot water. Dissolve the precipitate in hot hydrochloric acid. Make to a volume of approximately 25 cc, boil and again precipitate with ammonium hydroxid; filter, wash thoroughly with hot water, dry, ignite, and weigh as iron and aluminum oxids.¹ The filtrate is solution B.

(c) *Iron.*

Fuse the residue of iron and aluminum oxids with fused potassium hydrogen sulphate. This fusion takes but a few minutes and must not be continued beyond the time actually needed. When the fusion is complete it is set aside and allowed to cool. Add dilute sulphuric acid and heat the crucible until the fusion is dissolved. Evaporate on the water bath as far as possible; then heat gradually until fumes of sulphuric acid come off copiously. Dissolve in water and allow to stand on the water bath. Cool the solution, transfer to an Erlenmeyer flask, and make up to such a volume that it does not contain more than 2.5 per cent of free sulphuric acid. Hydrogen sulphid² is passed through the solution reducing the iron and precipitating the platinum contaminating the residue from the fusion. Filter and wash. Again pass through the solution hydrogen sulphid. Be sure that all the iron is reduced. Next expel the hydrogen sulphid by boiling, but at the same time pass through the solution a current of carbon dioxid, the removal of all hydrogen sulphid being found by occasionally testing the escaping gas with lead acetate paper. When hydrogen sulphid has been removed boiling is discontinued, the flask allowed to cool somewhat without discontinuing the current of carbon dioxid. The reduced iron is then titrated with a standard permanganate solution and calculated as iron.

If the amount of iron is less than 1 mg it may be determined colorimetrically, as follows:

Fuse the ignited precipitate of iron and aluminum oxids with potassium hydrogen sulphate, dissolve in water, and precipitate the iron and aluminum with ammonium hydroxid. Dissolve the precipitate from the filter paper in hydrochloric and nitric acids, dilute the solution, add ammonium sulphocyanate, and compare the color developed with that of calibrated color disks, or standards containing known amounts of iron.

(d) *Aluminum.*

Subtract the iron found as oxid from the original weight of iron and aluminum oxid, which in the absence of phosphates gives the weight of aluminum oxid. Calculate to aluminum.

(e) *Colorimetric determination of manganese.*

To from 50 to 100 cc of the water in a beaker add about 1 cc of strong nitric acid and approximately 0.02 gram of silver nitrate (10 cc of a solution of 2

¹ This is in the absence of phosphates. If phosphoric acid is present in small amounts it is precipitated with the iron and aluminum.

² Zinc may be used instead of hydrogen sulphid for reducing the iron.

grams per liter). If a precipitate of silver chlorid appears, more silver nitrate must be added until the chlorin is precipitated and as much as 0.02 gram of silver nitrate remains in solution. Filter from the silver chlorid, add 1 gram of ammonium persulphate to the filtrate, and place the beaker or flask containing the solution on the steam bath until a pink color develops (usually about 20 minutes). Compare the color developed with standards prepared by treating with nitric acid and ammonium persulphate solutions containing known amounts of manganese. To prepare a standard solution of manganese sulphate, weigh out 0.2877 gram of pure potassium permanganate, dissolve in a small amount of water, and add an excess of sulphuric acid; carefully reduce with oxalic acid and make up to 1 liter; 1 cc of this solution contains 0.0001 gram of manganese. If only a small quantity of manganese is present, determine it in the sodium carbonate precipitate which was extracted for bromin, iodin, arsenic, and boron (as given on p. 9, Bureau of Chemistry Circular 52). Dissolve the precipitate in nitric acid and treat with silver nitrate and ammonium persulphate, as given above.

(f) *Calcium, strontium, magnesium.*

Concentrate solution B to about 150 or 200 cc, and to this solution containing not more than 0.6 gram of calcium oxid or 1 gram of magnesium, calculated as pyrophosphate, add from 1 to 2 grams of oxalic acid and sufficient hydrochloric acid to clear the solution. Heat to boiling and neutralize with ammonium hydroxid, constantly stirring. Add ammonium hydroxid in slight excess and allow to stand for three hours, preferably in a warm place. Filter off the supernatant liquid and wash the precipitate by decantation once or twice with cold water. Dissolve precipitate with hydrochloric acid, dilute to from 100 to 200 cc, add a little oxalic acid, and precipitate as before. After standing three hours filter, wash with cold water,¹ dry, ignite, and blast and weigh as calcium and strontium oxids. The filtrate and washings are solution C.

Dissolve the above oxids with dilute nitric acid and test with the spectroscope for strontium. If strontium is found, transfer the nitric-acid solution to a small Erlenmeyer flask and evaporate to complete dryness on the steam bath. Heat at 150° to 160° C. for one or two hours until perfectly dry. Cool, add from 3 to 5 cc of a mixture of equal parts of absolute alcohol and ether. Cork the flask and allow to stand for 12 hours, with occasional shaking. Filter, wash with alcohol-ether mixture until a few drops of the filtrate evaporated on platinum foil or watch glass leaves no residue.

Dry the paper and precipitate. Dissolve the strontium nitrate with a few cubic centimeters of hot water. Add a few drops of sulphuric acid, then a volume of alcohol equal to the volume of the solution. Allow to stand 12 hours. Filter, ignite, weigh as strontium sulphate, and calculate to strontium. Test spectroscopically for absence of calcium. Subtract from the total oxids of strontium and calcium the strontium oxid equivalent to the strontium sulphate found. The difference is calcium oxid. Calculate to calcium. As a check on the calcium oxid, evaporate to dryness the filtrate from the strontium nitrate, dissolve the calcium nitrate in water, precipitate as oxalate, filter, wash, ignite, and weigh as calcium oxid.

(g) *Magnesium.*

Concentrate solution C to about 200 cc, add from 2 to 3 grams of di-ammonium hydrogen phosphate² and sufficient hydrochloric acid to clear the solution when the ammonium phosphate is all dissolved; when cold make slightly alkaline with ammonium hydroxid, constantly stirring. Add 1 to 2 cc excess of ammonium hydroxid. Allow to stand overnight. Filter off the supernatant liquid and wash three or four times by decantation with 2.5 per cent of ammonium hydroxid. Dissolve the precipitate in hydrochloric acid. Dilute to about 150 cc. Add a little di-ammonium hydrogen phosphate and precipitate with ammonium hydroxid as before. Allow to stand overnight, filter, wash free from chlorids, ignite, blast, and weigh as magnesium pyrophosphate; calculate to magnesium.

¹ Usually two or three washings are sufficient. Owing to the solubility of strontium oxalate excessive washing gives low results.

² Disodium hydrogen phosphate or sodium ammonium hydrogen phosphate may be used.

4. SULPHURIC ACID, SODIUM, POTASSIUM, LITHIUM.

(a) *Sulphuric acid.*

A preliminary examination should be made, using from 100 cc to 250 cc of the water to determine the quantity of sulphates. The alkali salts present can be approximated by calculating the amount of sodium necessary to combine with the excess of acids (chlorin, sulphuric, and bicarbonic acid) over the calcium and magnesium.

Evaporate such a quantity of the water that the weight of barium sulphate will not exceed 1 gram and the weight of the mixed chlorids will not exceed 0.5 gram. Acidify the quantity of water (usually from 1 to 5 liters) with hydrochloric acid. Evaporate to dryness in a platinum dish and remove silica by two evaporations as under 3 (a), page 77, using not more than 2 cc of hydrochloric acid for the final solution. Combine filtrate and washings from the silica determination. Concentrate to about 150 to 200 cc. Heat to boiling and precipitate with slight excess of 10 per cent barium chlorid, added very slowly, drop by drop, constantly stirring. Cover and allow to stand on the steam bath overnight. Filter, thoroughly wash the precipitate of barium sulphate with hot water, dry, ignite over Bunsen burner, and weigh. Calculate to sulphate (SO_4). The filtrate is solution E.

(b) *Sodium, potassium, lithium.*

Evaporate solution E to dryness in a platinum dish and ignite the residue to a very low redness to remove all traces of ammonium salts. Dissolve the residue in the dish with about 200 cc of water and precipitate with milk of lime or a solution of barium hydroxid. Boil, allow to stand half an hour, and filter off the insoluble magnesium hydroxid. Thoroughly wash the precipitate with hot water and combine the filtrate and washings. If the precipitate of magnesium is large, it is advisable to dissolve in a small amount of hydrochloric acid, evaporate to dryness, take up with water, and again precipitate with milk of lime or barium hydroxid as before. Concentrate the two filtrates and washings to about 200 or 250 cc. Add ammonium hydroxid and a sufficient quantity of ammonium carbonate to precipitate calcium and barium. Allow to stand on a steam bath for from one to two hours. Filter off the supernatant liquid, dissolve in hydrochloric acid, and precipitate as before and thoroughly wash with hot water. Evaporate filtrate and washings to dryness, dry and drive off the ammonium salts by gentle heat. Take up the residue with water; filter through a small filter, using as little wash water as possible; evaporate to a small volume and again precipitate with a drop or two of ammonium hydroxid and two or three drops of ammonium carbonate and oxalate. If any precipitate appears (which is not usually the case), filter and repeat the process. Evaporate the filtrate to dryness and drive off all ammonium salts by heating in platinum to a little below redness. Take up the residue with a little water, filter into a small platinum dish, add a few drops of hydrochloric acid, and evaporate to dryness. Dry in an oven, heat to a little below redness, cool in a desiccator, and weigh the combined chlorids of potassium, sodium, and lithium. Repeat the heating to constant weight. Dissolve the mixed chlorids with hot water, filter, and wash. Return the filter paper and small amount of residue usually found to the dish, dry, ignite, and weigh. The difference between the original weight of mixed chlorids and dish, and the weight of dish and small amount of residue equals the mixed chlorids. The combined chlorids are transferred to a small Erlenmeyer flask (50 or 100 cc capacity) and the solution evaporated nearly, but not quite, to dryness. Add about 30 cc of redistilled amyl alcohol. Connect flask, stopper of which carries a thermometer, with a condenser¹ and boil until the temperature rises approximately to the boiling point of amyl alcohol (130°C.), showing that all the water has been driven off. Cool slightly and add a drop of hydrochloric acid to convert small amounts of lithium hydroxid to lithium chlorid. Connect with the condenser and continue the boiling to drive off again all water and until the temperature reaches the boiling point of amyl alcohol. The content of the flask at this time is usually from 15 to 20 cc. Filter through a small paper or a

¹ The amyl alcohol may be boiled off without the use of a condenser, but the vapors are very disagreeable.

Gooch crucible into a graduated cylinder and note exact quantity of filtrate which determines the subsequent correction. Wash the precipitate with small quantities of dehydrated amyl alcohol. Evaporate the filtrate and washings in a platinum dish to dryness on the steam bath, dissolve the residue in water, and add a few drops of sulphuric acid. Evaporate on a steam bath and expel the excess of sulphuric acid by gentle heat over a flame. Repeat until carbonaceous matter is completely burned off. Cool and weigh the dish and contents. Dissolve in a small quantity of hot water, filter through a small filter, wash and return filter to dish; ignite and weigh. The difference between the original weight of dish and contents and the weight of the dish and small amount of residue equals the weight of impure lithium sulphate.¹ From this weight subtract 0.00113 gram for every 10 cc of amyl alcohol filtrate² on account of the solubility of sodium and potassium chlorids in amyl alcohol. Calculate lithium from the corrected weight of lithium sulphate. Dissolve the mixed chlorids from flask and filter with hot water, evaporate to dryness, ignite gently to remove amyl alcohol, filter and thoroughly wash; concentrate the filtrates and washings to from 25 to 50 cc. Transfer to a porcelain dish and add platinic chlorid solution sufficient to convert sodium and potassium to platinic chlorids and evaporate to dryness. Treat the residue with 80 per cent alcohol and filter and continue washing until the excess of platinum chlorid and sodium platinic chlorid has been removed.

Dry the filter, dissolve the residue with hot water, and transfer to a weighed platinum dish. Evaporate on the steam bath, dry in the oven at 100° C. for 30 minutes and weigh as potassium platinic chlorid; calculate to potassium chlorid. To the weight of potassium chlorid add 0.00051 gram for every 10 cc of amyl alcohol used in the extraction of the lithium chlorid, which corrects for the solubility of the potassium chlorid in amyl alcohol. Calculate to potassium.

The weight of sodium chlorid is found by subtracting the combined weights of lithium chlorid and potassium chlorid (corrected) from the total weight of the three chlorids. Calculate sodium chlorid to sodium.

5. PHOSPHORIC ACID.

[As in Circular 52, p. 8.]

6. CHLORIN.³

To 100 cc of the water add a few drops of phenolphthalein. If a red color is shown titrate the carbonates thus indicated to bicarbonates with tenth or twentieth-normal sulphuric acid. (Add at the rate of a drop every few seconds until the red color disappears.) Add 1 cc of potassium chromate solution⁴ (in the beginning if a red color is not shown with phenolphthalein) and titrate the chlorids with a standard solution of silver nitrate (1 cc=1 mg of chlorin). If iodids and bromids are found make the equivalent correction. If sufficient chlorids are present to consume more than 25 cc of the standard silver nitrate for 100 cc of the water, they should be determined by precipitating in nitric acid solution and weighing the silver chlorid found.

7. NITRIC ACID.⁵

Transfer to a porcelain dish 100 cc of the water or if the nitrates are high, such a volume as will contain about 1 mg of nitrogen. Add sufficient twentieth-normal sulphuric acid to nearly but not quite neutralize all the alkalinity. Add standard silver sulphate free from nitrate (4.3969 grams per liter, 1 cc equals 1 cc of standard silver nitrate solution equals 1 mg of chlorin per

¹ The purity of the lithium sulphate should be tested by adding small amounts of ammonium phosphate and ammonium hydroxid, which will precipitate any magnesium present with the lithium sulphate. Any precipitate appearing after standing overnight should be collected on a small filter and weighed as magnesium pyrophosphate, calculated to sulphate and subtracted from the weight of impure lithium sulphate.

² Exclusive of the amyl alcohol used in washing residue because of the slight solubility of small mixed chlorids in amyl alcohol.

³ Substitute for chlorin method given in Cir. 52, p. 6.

⁴ Dissolve 5 grams of potassium chromate in 100 cc of distilled water, add a solution of silver nitrate till a slight permanent red precipitate is produced. After standing several days siphon off the clear solution.

⁵ Substitute for the method given in Cir. 52, p. 4.

cubic centimeter) precipitating all but about 0.5 mg of the chlorin. Heat to boiling, allow to settle, or add a little aluminum cream, filter and wash with small amounts of hot water. Evaporate the filtrate to dryness in porcelain; when cold add 2 cc of disulphonic acid¹ reagent, rubbing with a glass rod to insure intimate contact. Dilute with distilled water and add slowly ammonium hydroxid until the maximum color is developed. Transfer to a colorimetric cylinder, filtering if necessary, and compare with a standard potassium nitrate solution (containing 0.01 mg nitrate in 1 cc) which has been treated in like manner with phenol disulphonic acid reagent. Compare in the usual manner and record as nitrogen in the form of nitrates.

S. FREE AND ALBUMINOID AMMONIA.²

Connect a large flask of about 1.5 liters capacity with an upright bulb condenser by means of a rather large glass tube and a soft rubber stopper or a recently extracted cork stopper. Place in the flask 5 cc of a concentrated solution of sodium carbonate and 500 cc of ammonia-free water. Distil off in 50-cc Nessler jars until no further traces of ammonia are obtained, and continue the distillation until the solution in the flask has been reduced to about 200 cc. Cool slightly, add 500 cc of the water under examination, and distil³ into 50 cc Nessler jars until ammonia ceases to be given off. Four or five jars are usually sufficient. Nesslerize and compare the depth of color with other jars containing known amounts of standard ammonium chlorid solution (0.01 mg of ammonia (NH₃) in 1 cc) made up to 50 cc with ammonia-free water and Nesslerized in a similar manner. Report as ammonia (NH₃). Cool the flask and add 50 cc of recently boiled permanganate solution (prepared by dissolving 200 grams potassium hydroxid and 8 grams of potassium permanganate in 1 liter). Distil³ off into 50-cc Nessler jars until ammonia ceases to come off. Nesslerize and compare in a similar manner as for the determination of free ammonia.

9. PROMIN, IODIN, ARSENIC, AND BORON.

[Circular 52, pp. 9, 10, and 11, unchanged.]

10. CARBONIC (CO₂) AND BICARBONIC (HCO₃) ACIDS.

To 100 cc of the water add a few drops of phenolphthalein and if a pink color is produced titrate with twentieth-normal acid potassium sulphate or sulphuric acid, adding a drop every two or three seconds, until the red color has disappeared. Multiply by the factor 0.003, which gives the grams of carbonic acid in 100 cc. To the colorless solution from this titration or to the original solution if no color is produced with phenolphthalein, add one or two drops of methyl orange and continue the titration without refilling the burette and note the total reading. If carbonic acid is absent, multiply the total burette reading by the factor 0.00305, which gives the value of bicarbonic acid in grams per 100 cc. If carbonic acid is present, multiply the reading with phenolphthalein by 2 and subtract from the total reading of the burette. Multiply the difference by the factor 0.00305, which gives the bicarbonic acid in grams per 100 cc. Multiply the result by 10 to convert to grams per liter.

11. FREE CARBON DIOXID.

[As in Circular 52, p. 11.]

12. METHOD OF REPORTING RESULTS.

[As in Circular 52, p. 12.]

¹ Prepared by dissolving 25 grams of pure white phenol in 150 cc of chemically pure sulphuric acid, concentrated, and 75 cc of fuming sulphuric acid (18 per cent SO₃) and heating at 100° C. for two hours.

² Substitute for methods for free and total ammonia, Cir. 52, p. 5.

³ At the rate of one tube full in 15 minutes.

REPORT OF COMMITTEE A ON RECOMMENDATIONS OF REFEREES.

By J. P. STREET, *Chairman.*

(Nitrogen, potash, phosphoric acid, soils, inorganic plant constituents, insecticides, and water.)

PHOSPHORIC ACID.

It is recommended—

(1) That the following method of analysis [Wagner method, see p. 12] be adopted provisionally pending further study and the gathering of more complete data in regard to field and pot experiments.

Adopted.

(2) That further work be done with the citrate of ammonia magnesia mixture method [see p. 12] and the official volumetric method, using the Wagner method of making the citric solution of the slag, as given under recommendation 1.

Adopted.

(3) That the referee on phosphoric acid for 1912 study the conductivity method for making the neutral ammonium citrate solution. (See J. Amer. Chem. Soc., 1911, 33: 711; J. Ind. Eng. Chem., 1911, 3: 559.)

Adopted.

NITROGEN.

It is recommended—

(1) That the study of methods for the determination of available nitrogen be continued, and that the alkaline permanganate and neutral permanganate methods as now modified be studied as applied to crude stock and to commercial fertilizers.

Adopted.

(2) That the recommendation made on page 129 of Bulletin 116¹ be studied with a view to its applicability to complete fertilizers and meat products.

Adopted.

This recommendation reads as follows: "(5) That on page 7 of Bulletin 107, after insert recommended under (4), add the following: "Approximately 0.7 gram of mercuric oxid, or its equivalent in metallic mercury, may also be added, before the addition of the potassium sulphate, but if mercury be used potassium sulphid must be employed, as in the Kjeldahl method, in the distillation."

(3) Mr. E. L. Baker's resolution to the effect that Salle's method for the determination of nitrogen in commercial nitrates be referred to the referee for 1912 for trial was adopted. The method is given on page 28.

SOILS.

It is recommended—

(1) That the methods approved and referred to the association for final action in 1910, under recommendations 1, 2, and 3, page 3 of Circular 52, be finally adopted as official.

Adopted.

These recommendations read as follows:

(1) That the modified J. L. Smith method for total potassium be made an official method of this association, and that the clauses "and transfer to a filter" and "after washing free of chlorids" in this method be replaced by the following sentence: "After washing four or five times by decantation with hot water, throw on the filter and wash well, 250 to 300 cc of wash water being sufficient."

(2) That the magnesium nitrate method for total phosphorus be made an official method of this association.

¹ All bulletin references are to Bureau of Chemistry series, United States Department of Agriculture.

(3) That the sodium peroxid fusion method for total phosphorus be made an official method.

(2) That the referee on soils continue his research for a method or methods that will permit of an accurate estimation of the lime requirements of soils.

Adopted.

(3) That the Rather method (p. 52, see also J. Ind. Eng. Chem., 1911, 3:660) for humus be further studied with a view to substituting it for the present official method.

Adopted.

(4) That the modified volumetric cobalti-nitrite method be further studied in its application to soils (J. Ind. Eng. Chem., 1909, 1:302; Bul. 137, p. 25).

Adopted.

POTASH.

It is recommended—

(1) That the Drushel volumetric cobalti-nitrite method be further studied in its application to mixed fertilizers (Bul. 132, p. 21).

Adopted.

(2) That a further study of the gravimetric cobalti-nitrite method be made in the case of mixed fertilizers, using the modification suggested by Itano of precipitating the phosphates with milk of lime before adding the cobalti-nitrite reagent.

Adopted.

(3) That the proposed modification of the official method (p. 29) be approved and be referred to the association for final action in 1912.

Adopted.

(4) That the factors for calculating potash from potassium platonic chlorid (Bul. 107, Rev., p. 12) be revised to read as follows:

Under "(c) Factors," read "For the conversion of potassium platonic chlorid to potassium chlorid, use the factor 0.3067; to potassium sulphate, 0.3585; to potassium oxid, 0.1938." (This change is made in accordance with the new atomic weights.)

Adopted.

INORGANIC PLANT CONSTITUENTS.

It is recommended—

(1) That the molybdate method in the form in which it is now presented for the separation of ferric and aluminic oxids in an ash solution be approved, with a view to its adoption as an official method in 1912. [See p. 61.]

Adopted.

(2) That the oxalate method for the separation of ferric and aluminic oxids in an ash solution be further studied on a synthetic solution, with a view to its final adoption by the association. [See p. 61.]

Adopted.

(3) That cooperative work be done on the molybdate method as extended and described in the 1911 report for the separation of calcium and magnesium in an ash solution. [See p. 65.]

Adopted.

(4) That cooperative work be done on the method entitled "The determination of total sulphur in organic matter," described by Herman Schreiber in Circular 56.

Adopted.

WATER.

It is recommended—

(1) That the methods as proposed for the examination of waters (see Cir. 52, pp. 4 to 14) be accepted as the provisional methods of the association.

Adopted.

INSECTICIDES.

It is recommended—

(1) That the chromate method (Method II) for total lead oxid in lead arsenate be adopted as official (Bul. 137, p. 41, and Cir. 66, p. 2).

Recommendation adopted and referred to association for final action in 1912.

(2) That the method for water-soluble arsenic oxid in lead arsenate be further studied as regards time of standing for the solution of soluble arsenic, and the effect of different temperatures thereon (Bul. 107, Rev., p. 240).

Adopted.

(3) That the method for total sulphur in lime-sulphur solutions (Bul. 107, Rev., p. 34) be changed as follows: Under "2. Determination," line 1, after "measure" insert "and accurately weigh"; after "sample" strike out "in" and insert a comma and the words "transfer to"; and that the method as thus changed be recommended for final adoption as official in 1912.

Adopted.

(4) That the gravimetric method for sulphur as sulphids and polysulphids in lime-sulphur solutions, as given in the referee's report [p. 70], be adopted as official.

Recommendation adopted and referred to the association for final action in 1912.

(5) That the volumetric method for sulphur occurring as thiosulphate in lime-sulphur solutions, as given in the referee's report [p. 70], be adopted as official.

Recommendation adopted and referred to the association for final action in 1912.

(6) That the method given [by the referee] for sulphur occurring as sulphates and sulphids in lime-sulphur solutions [p. 70] be changed to read as follows and as changed be adopted as official:

Sulphur as sulphate and sulphite.—To the solution from the determination of thiosulphate add 2 or 3 drops of hydrochloric acid, warm on steam bath, precipitate with barium chlorid solution, stirring vigorously for several minutes; let stand in the cold overnight, filter, and obtain weight of barium sulphate. From this weight calculate sulphur.

Recommendation adopted and referred to the association for final action in 1912.

The following recommendations, which were adopted by the association in 1909, are hereby renewed for final action:

(7) That "Method II" for total arsenious oxid in London purple, as given in Bulletin 107, Revised, page 29, be dropped from the methods of analysis.

Adopted.

(8) That "Method II" for total arsenic oxid in London purple, as given in Bulletin 107, Revised, page 29, be dropped from the methods of analysis.

Adopted.

The three following recommendations, adopted by the association in 1910, are hereby renewed for final action:

(9) That "Method I" for total arsenious oxid in London purple, as given in Bulletin 107, Revised, page 28, be adopted as official.

Adopted as official.

(10) That "Method III" as proposed by the referee in 1909 (Bul. 132, p. 43) for total arsenic oxid in London purple be adopted as official and designated as "Method II."

Adopted as official.

(11) That the Gatehouse method (Sutton's Volumetric Analysis, 9th ed., p. 201; Cir. 10, Rev., p. 6) for the determination of chlorin in cyanids be adopted as official.

Adopted as official.

(12) That the provisional methods for the analysis of lead arsenate (Bul. 107, Rev., p. 239) be changed in accordance with recommendation 7 of the referee in 1910 (Bul. 137, p. 47), and, as changed, adopted as official.

Recommendation adopted and referred to the association for final action in 1912.

SEPARATION OF NITROGENOUS BODIES (MILK AND CHEESE).

It is recommended—

(1) That the Folin method¹ for the determination of ammonia be further studied. (Zts. physiol. Chem., 1902-3, 37:161.)

Adopted.

(2) That the Van Slyke method for the determination of amino acid nitrogen be further studied. (D. D. van Slyke, Ber. d. chem. Ges., 1910, 43 (3):3170.)

Adopted.

REPORT OF COMMITTEE ON AMENDMENTS TO THE CONSTITUTION AND BY-LAWS.

By L. L. VAN SLYKE, *Chairman*.

(1) The following resolution, introduced by W. A. Withers, was favorably reported by the committee and was adopted by the association:

Resolved, That compliance with section 4 of the constitution necessitates the appointment of referees and associate referees by the retiring, rather than by the incoming, executive committee: *Resolved further*, That the secretary of the association is hereby requested to provide a place on the program for the announcement of the appointment of referees and associate referees.

(2) The following resolutions were introduced by O. M. Shedd and referred to the committee, with the results stated:

(a) *Resolved*, That section 4 of the constitution of this association be changed to read as follows:

There shall be appointed by the executive committee at the regular annual meeting from among the members of the association a referee, and, after consultation with him, such associate referees for each of the subjects to be considered by the association as that committee may deem appropriate.

The committee reported unfavorably on the adoption of this resolution as an amendment to the constitution, but moved that a standing rule be adopted to the effect that the executive committee consult with each referee in the appointment of associate referees.

The report of the committee was adopted.

(b) *Resolved*, That a new section be added to the by-laws to follow section 4, and to read as follows:

As soon as possible after the annual meeting of the association each retiring referee shall transmit a copy of his report and recommendations, together with a statement of the action taken by the association upon the same, to the referee for the next year.

The committee reported this amendment favorably as an addition to section 4, and the report was adopted:

(c) *Resolved*, That paragraph 3 of the by-laws be amended by adding the following words:

That the referee on each subject be ex officio member of the subcommittee on recommendations of referees which passes upon his recommendations, but only for the purpose of such action as relates to his own work.

¹ See referee's report, p. 185, for recent modification by Folin.

The committee reported the resolution unfavorably, but stated that it was the sense of the committee that, except when impossible, opportunity should be given each referee for full consultation with the committee on recommendations before final action by the committee on the recommendations of the referee.

The report of the committee was adopted.

Brief verbal reports were made by the chairmen of the following committees:

Committee on appropriation.—Mr. Street, as chairman, reported that no meeting had been held, and since the Proceedings were to be published by the Department of Agriculture and the dues now paid by the members covered all other expenses he asked that the committee be discharged. After some discussion, however, the report of the committee was accepted by the association on a motion by Mr. Frear, but the committee was continued.

Committee on food standards.—Mr. Frear, as chairman, made a report of progress, stating that the committee had held a meeting in August in Duluth at which a special line of work was taken up and would be pushed as rapidly as possible.

Committee on participation in the Eighth International Congress of Applied Chemistry.—Mr. Street, as chairman, stated that he thought that the committee no longer had any function to perform, inasmuch as the ground was well covered by Mr. Cameron's and Mr. Bigelow's committees. It was urged that the members of the association cooperate with the various sections and insure that the association be adequately represented on the program of the congress. The effect of the ruling that no papers presented at the congress could be published elsewhere was also mentioned, and attention called to the fact that in the preliminary announcement of the congress the association had not been included. The chairman asked that the committee be discharged, and upon motion the report was accepted and the committee discontinued.

Committee on the testing of chemical reagents.—Mr. Kebler, as chairman, made the following brief report of progress: At the last meeting the committee reported on the desirability of using certain designations in connection with chemical reagents. These recommendations were also forwarded to the chairman of a similar committee of the American Chemical Society, but they have not been discussed as fully as the committee hoped they might be.

It is fairly well established that the designation "C. P." serves no good purpose except in a few special instances. The result is that most manufacturers are rapidly eliminating it from their price lists; in fact, some have done so completely. It was intended to present at this meeting the specifications referred to in the recommendations last year for various chemical reagents with the possibility of some action. Unfortunately this was impossible, but it is believed that the specifications can be presented at the next meeting. It is urged that the subject of chemical reagents be given more consideration by the association in the future than has been the case in the past.

The report of the committee was received.

On motion by Mr. Frear the association authorized the secretary-treasurer to pay the balance of a bill owing by the food standards committee for printing, amounting to \$31.03.

The association adjourned.

SECOND DAY.

TUESDAY—MORNING SESSION.

REPORT ON FOOD ADULTERATION.

By A. S. MITCHELL, *Referee.*

The past year has been an active one both in the perfecting of new methods and in the collaborative trying out of the present standards. I shall leave the details of the work for discussion by the associates who have so ably and disinterestedly accomplished it, and will but touch upon such points as seem of interest to all.

The referee on cereals has made a good beginning on methods for the analysis of wheat flour, but we ask only for the adoption of such portions as seem most free from criticism.

The referee on vinegar recommends a partial revision of methods. The Ross method is offered for glycerin as an index of purity of cider vinegar. This is novel, but when it is noted that glycerin is a congener of alcoholic fermentation and is separated from low wines in their distillation, while it remains in the final product in undistilled vinegars, its possibilities are apparent.

The referee on fats and oils has conducted a study on beef fat in lard. Tests by the Belfield method proved less satisfactory than by the Emery method, a method based on the melting point of the crystallized glycerids.

Collaborative work on the methods for the separation and identification of artificial colors has shown a reliability almost surprising, considering the complexity of the subject.

Extensive work has also been done on the flavoring extract methods. Improvements in methods for vanilla extract are reported which result in saving time and increasing accuracy. The unreliability of certain other methods has been demonstrated.

Under spices, the study of paprika has brought out a new characteristic, the remarkably high index of refraction of its oil. The collaborative work on the crude fiber method as applied to prepared mustard indicates the reliability of the present method.

A large amount of work has been done on ketchups. Three collaborators have made lengthy analyses involving 36 determinations on each of the three samples sent out. It will be noted that food chemists are looking less upon the wine when it is of varied hue and are more closely scrutinizing the tomato when it is overripe. This study has emphasized the work of Bacon and Dunbar as to the value of lactic and citric acid ratios as an indication of decay in tomato products. Citric acid, which is present in sound, ripe tomatoes, rapidly disap-

pears upon decomposition, with a corresponding development of lactic acid. The work done upon the methods offered shows the need of their further study.

The referee on dairy products reports a method for obtaining fat from ice cream and similar foods in sufficient quantity to admit of its thorough examination.

Progress is also reported in the examination of methods for the determination of caffeine in tea and coffee. The question of coloring matter in tea came up too late for action this year. For the coming year, it is suggested that the referee make this a special study. A draft of methods has been issued by the United States Treasury Department, but more searching microscopical methods seem desirable.

A method is needed for the determination of diastase in fermented liquors for which diastatic action is claimed. Standard methods are also needed for the examination of beverages, particularly so-called soft drinks, and for the examination of coatings and glazings in confectionery.

The desirability of the appointment of a referee on methods for the determination of arsenic, lead, tin, copper, barium, and the heavy metals is obvious.

Microscopical methods are gaining prominence in the examination of prepared foods, spices, coloring of tea, etc., and their development would seem to warrant the appointment of a special referee.

The work of the food analyst is increasing in complexity and ramifying in new directions. This calls for an increased loyalty and sacrifice of time from the food chemists of this association, to enable us to take up the varied, and, too frequently, lengthy, methods and try them out, ever keeping in mind accuracy, simplicity, and speed. In concluding, I wish to thank my associates for the interest they have shown and the time and attention which they have given to this work.

REPORT ON SPICES.

By R. W. HILTS, *Associate Referee*.

The work done this year falls under the two headings of ether extract of paprika and crude fiber in prepared mustard.

PAPRIKA EXTRACT.

In accordance with last year's recommendations, the associate referee has made some further study of the ether extract of paprika and of the method of drying it. No samples were sent out, as the nature of the work rendered it unsuitable for cooperative investigation. The work was divided into two parts:

(A) Some experiments were made on the drying of ether extract of paprika under the conditions of the provisional method, last year adopted, as compared with drying for the same periods in a current of dry hydrogen. For this purpose a sample of Hungarian paprika, which appeared entirely normal, was dried over sulphuric acid and extracted with pure dry ether. The ether solution was filtered and four equal portions of it measured into glass-stoppered flasks and the ether distilled off as usual. All four flasks were dried side by side in the same water oven for two successive half-hour periods. Two were dried in air, as in the provisional method, but the other two were fitted with a suitable arrangement of two-hole stoppers and glass tubes by means of which a rapid current of hydrogen, dried by sulphuric acid, was circulated through them. This passed in at the top and out at the bottom through the longer

tube, thus assuring rapid drying and displacement of the ether vapor. The results are as thus tabulated:

Comparison of drying paprika extract in air and in hydrogen.

Time.	Weight—			
	Drying in air.		Drying in hydrogen.	
After one-half hour.....	Gram. 0.3024	Gram. 0.3055	Gram. 0.3038	Gram. 0.3046
After 1 hour.....	.3021	.3053	.3034	.3043

The data indicate that drying proceeded with equal speed under both conditions and that the weight changes, though slight, were practically identical. The iodine numbers also agree very well indeed, 133.3 and 132.7 on the samples dried in air, and 133.9 and 133.1 for those dried in hydrogen. The values of the two methods overlap, and the extreme differences are insignificant, as they are well within the range of experimental error. Hence it does not appear that the ether extract of paprika is appreciably oxidized by one hour's heating in air in the water oven under the conditions of the provisional method. Excessively long heating will undoubtedly change the extract and give lower iodine numbers, as shown by Seeker¹ and Lowenstein and Dunne,² but such heating is unnecessary, using pure, dry, freshly distilled ether. The referee has never found more than an hour's heating necessary. There does not seem, then, any reason for supplanting the present simple method by anything more cumbersome.

(B) For the purpose of making a further study of paprika extract, with a view to detecting foreign oils other than olive, a considerable quantity of the oil was prepared. By courtesy of the Bureau of Chemistry, the referee was furnished with a large sample of whole Spanish paprika, or pimenton. The fruit was whole, unbroken, and in good condition. The pods were globular, about 2 inches in diameter, and were strung on strings. The stems were separated and rejected and the sample ground in the laboratory and examined by the methods officially adopted. The composition of the sample and the results were as follows:

Stems	108.5 grams (8.89 per cent)
Seeds and placenta.....	429.0 grams (35.17 per cent)
Shells	682.5 grams (55.94 per cent)

Analytical determinations:

Ether extract (per cent)	11.40
Iodine number.....	136.0
Total ash (per cent).....	7.05
Ash insoluble in acid (per cent).....	0.07

From the data available the values appear to be normal. After rejection of the stems the sample contained 38.6 per cent of seeds and placenta and 61.4 per cent of shells. It had a good red color after grinding.

Eight hundred grams of the material were packed in a percolator and extracted by slow percolation with redistilled petroleum ether boiling below

¹ U. S. Dept. Agr., Bureau of Chemistry Bul. 137, p. 82.

² J. Ind. Eng. Chem., 1910, 2: 139.

55° C.¹ Percolation was continued until most of the oil was removed. The oil was freed from the last of the petroleum ether by heating in a flask immersed in boiling water, under a partial vacuum, meanwhile admitting a slow current of dry hydrogen to displace the ether and prevent oxidation. The oil was finally filtered at a moderate temperature. The yield was about 75 grams or 9.4 per cent. The extract was a rather viscous oil, fluid at all ordinary temperatures and of a very intense red color, almost black in bulk, and with an odor suggestive of the spice. It was examined with the following results:

Specific gravity 15.6°/15.6° C.....	0.9322
Index of refraction at 40° C.....	1.4858
Index of refraction at 15.6° C.....	1.4953
Iodin number.....	137.9
Reichert-Meissl number.....	0.82
Solid fatty acids (per cent).....	10.83
Acetyl value (filtration method).....	21.0
Acetyl value (corrected for soluble acids).....	9.45

The absorption spectrum, in ether solution, possessed no bands and showed nothing distinctive. The intense color of the oil interferes so much with the indicator that the referee has not as yet succeeded in determining the saponification number. Ordinary methods of bleaching were only partly successful, and attempts to use an external indicator were unsatisfactory. It seems that any method of bleaching sufficiently rigorous to be successful might materially alter the oil.

The iodine number of the oil thus prepared agrees well with that found in the preliminary examination by the provisional method, pointing to the similarity of the oil to that extracted by ethyl ether. It is probably purer than an ether extract would be. Contrary to the figures of Szigeti,² published by the associate referee last year, neither the acetyl value nor the Reichert-Meissl number appears to be higher than those of the ordinary oils and fats. Strict comparison with his results is of course impossible, since his method of preparing the extract is unknown. Partial oxidation and hydrolysis might account for his low iodine numbers and high acetyl values. The index of refraction, however, is remarkably high, even above Szigeti's values, which were 1.489-1.490 at 15° C. Of all the constants determined the index of refraction is the only one, aside from the iodine number, which seems to be promising for the detection of foreign oils. It has also the advantage of requiring little material. The determination of this constant on numerous samples is accordingly desirable in order to observe its range of variations and thus to test further its value as a criterion of purity.

CRUDE FIBER IN PREPARED MUSTARD.

Last year's recommendation for the comparative study of the determination of crude fiber, with and without preliminary drying and extraction of fat, was made with special reference to prepared mustard. This year's referee on condiments other than spices kindly waived any interest he might have, and accordingly a large sample of prepared mustard was procured from a reputable grinder who stated that it was ground from the whole seed only. It was mixed

¹ Petroleum ether was chosen in preference to ethyl ether because of the practical difficulties of drying the large mass of material and keeping it dry, if dry ether was to be used. A preliminary experiment indicated that the iodine numbers of oils extracted by both solvents are practically the same and that hence the oils must be of nearly the same composition.

² U. S. Dept. Agr., Bureau of Chemistry Bul. 137, p. 85.

with particular care, and eight samples were sent out with the following instructions. Method II, with preliminary drying and fat extraction, was suggested by Mr. L. M. Tolman as having been tried in the Washington Food Inspection Laboratory. Method III, involving previous removal of the fat by washing with alcohol and ether without drying, was suggested by the associate referee.

INSTRUCTIONS TO COLLABORATORS.

Determine crude fiber by each of the three methods below. Also determine moisture in the original sample by the official method, and also moisture in the dried, and the ground air-dry sample in Method II. Determine ether extract in the air-dry sample in Method II, this being incidental to the crude fiber determination, and, for comparison, determine ether extract by the official method (I). The moisture determinations are indispensable. Use particular care in sampling. Transfer to a larger receptacle if necessary, and mix thoroughly with a spoon before removing each portion for analysis. Report all actual results obtained on the fresh and air-dry sample and also report crude fiber and ether extract calculated to dry substance.

Method I (official).

(Bul. 107, Rev., pp. 167-168; Proceedings A. O. A. C., 1905, Bul. 99, p. 73.)

Solids.—Dry 5 grams in a flat-bottomed platinum dish on a water bath until the mixture appears dry, and finally dry to constant weight at 100° C. in a water oven. First distribute the sample evenly over the bottom of the dish with a little water.

Crude fiber.—Follow the official method as outlined (Bul. 107, Rev., p. 168), remembering the additional directions last year adopted: "The fiber, however, should finally be washed successively with alcohol and ether until all fat is removed." Be particularly careful to break up thoroughly all lumps by shaking as directed. Stopper the flask and shake vigorously if necessary. The first filtrations may be made on paper or other convenient filter. A circle of closely woven linen in a 4-inch Buechner funnel with light suction gives a very rapid and satisfactory filtration. The linen circle is then spread out on the side of a short-stem 6-inch funnel, and the fiber washed back into the flask by means of a policeman and a wash bottle containing the hot 1.25 per cent alkali. The last filtration should be made on paper as officially directed. For this an 11 cm S & S blue ribbon paper is convenient and rapid. All weighings of paper and crude fiber must be made in weighing bottles.

Ether extract.—Follow the official method. Use a lead bottle cap or a Hoffmeister schaeleschen for drying the sample and finish the drying in the hot-water oven.

Method II.

Preparation of sample.—In an 8-inch porcelain evaporating dish spread out 100 grams of the sample and dry down on the steam or water bath. Finally dry in a vacuum oven, or if this is not available, dry for 3 to 4 hours more in a water oven. Let stand in the air for some hours to become air-dry; then scrape out of the dish and grind in a small drug mill to pass a 40-mesh sieve.

Moisture in air-dry sample.—Dry about 2 grams in a flat-bottomed dish in the water oven.

Ether extract.—Weigh out 2 grams of the air-dry sample, inclose in a folded 11 cm hardened filter paper, dry somewhat and extract in a Knorr or other suitable extraction apparatus for 16 hours with anhydrous ether.

Crude fiber.—Use residue from the ether extraction, and proceed according to the official method (Bul. 107, Rev., pp. 56, 164). Observe the comments on filtration made above. Final washing with alcohol and ether is unnecessary and is to be omitted.

Method III.

Crude fiber.—Weigh out 8 or 10 grams in a small beaker and add strong alcohol to a volume of about 75 cc. Allow to stand 15 to 20 minutes with occasional stirring and then filter through an 11 cm S & S hardened filter paper, transferring completely to the filter. Wash on the paper two or three times with alcohol and then 6 times with ether or until all fat is removed. Allow to drain, but not to dry or cake, and then rinse into the 500 cc Erlenmeyer flask with a little of the cold 1.25 per cent acid. Stopper, shake, make up to 200 cc with boiling acid and bring to a boil and boil gently for 30 minutes. Foaming

may occur until the ether is all expelled, hence the flask had best be simply covered with a watch glass, which permits blowing into it by means of a glass tube if the foam approaches the top. Continue the determination as under instructions for the official method, except that final washing with alcohol and ether is omitted.

The preliminary washing with alcohol and ether can also be conveniently performed by aid of the centrifuge, shaking the samples up in stoppered tubes 6 in. \times 1 in., then centrifuging and decanting off through the hardened filters, to which the solid material is finally transferred by means of ether.

Five collaborators made reports. Their names are as follows, the numbers indicating their results in the tables: (1) M. Boyle, Washington, D. C.; (2) A. W. Hanson, Kansas City, Mo.; (3) C. W. Harrison, Washington, D. C.; (4) R. W. Hilts, Philadelphia, Pa.; (5) H. E. Sindall, Philadelphia, Pa.; (6) C. R. Smith, New York, N. Y.

Cooperative results on solids and ether extract.

Analyst.	Solids.		Ether extract.			
	Method I.	Method II.	Method I.		Method II.	
	Original.	Air-dry.	Original.	Dry basis.	Air-dry.	Dry basis.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
1.....	17.53	90.18	3.63	20.74	16.14	17.90
	17.47	90.12	3.64	20.80	16.07	17.83
2.....	17.83	93.44	3.0	16.80	15.21	16.27
	17.86	93.46	2.9	16.24	15.15	16.21
3.....	17.66	93.83	3.47	19.62	16.27	17.34
	17.71	93.83	3.42	19.34	16.16	17.22
4.....	17.87	94.44	2.92	16.34	16.48	17.45
	17.87	94.40	2.93	16.39	16.47	17.44
5.....	17.54	95.77	3.15	17.96	17.34	18.05
	17.54	96.32	3.05	17.39	17.46	18.18
6.....	17.33	92.66	3.11	17.80	16.51	17.82
	17.61					
Average.....	17.65		3.20	18.13		17.43

¹ Three additional determinations gave 2.90 per cent, 2.94 per cent and 2.95 per cent of ether extract. Both Knorr and Soxhlet extractors used.

Cooperative results on crude fiber.

Analyst.	Method I.		Method II.		Method III.	
	Original.	Dry basis.	Air-dry.	Dry basis.	Original.	Dry basis.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
1.....	1.27	7.24	6.61	7.33	1.21	6.91
	1.24	7.13	6.74	7.47	1.19	6.80
			¹ 5.91	¹ 6.55		
			¹ 5.93	¹ 6.58		
2.....	1.19	6.67	6.8	7.27	1.38	7.73
	1.26	7.06	6.4	6.85		
3.....	1.085	6.14	6.99	7.45	1.115	6.31
	1.035	5.85	7.03	7.49	1.117	6.32
4 ²	1.09	6.10	6.62	7.01	1.02	5.71
	1.06	5.94	6.66	7.05	0.97	5.43
			6.83	7.23	1.02	5.73
5.....	1.08	6.16	7.15	7.44	0.95	5.42
	1.02	5.81	7.13	7.42	0.93	5.30
6 ³	1.48	8.47	7.59	8.19	1.30	7.44
	1.54	8.81			1.34	7.67
Average.....	1.19	6.78		7.24	1.13	6.40
Maximum.....	1.54	8.81		8.79	1.38	7.73
Minimum.....	1.02	5.81		6.55	0.93	5.30

¹ Values indicated were obtained by making both filtrations on linen and finally washing into a gooch for drying and ashing.

² Also found 1.41 per cent of salt.

³ Analyst 6 made all filtrations on linen, finally washing into a large platinum dish for drying and ashing.

COMMENTS BY THE COLLABORATORS.

Mr. Boyle finds filtration and drying on paper tedious and much prefers to make both filtrations on cloth, finally washing the fiber into a gooch for drying and ashing. The second set of results under Method II were thus obtained and are unaccountably lower than the others.

Mr. Harrison notes the fairly good agreement between Method I and III and the higher results by II. He sees no apparent benefit in the preliminary treatment with alcohol and ether in Method III except more rapid filtration from the acid, which, however, is offset by the troublesome frothing on first boiling. The final washing with alcohol and ether in the official method he considers a decided advantage as facilitating drying. He prefers Method I to either of the others as being easiest of manipulation, and believes it should give satisfactory and comparable results by different analysts, when followed as outlined. He adds, "I also find that the 11 cm S & S blue ribbon papers, on which you suggest that the filtration be made, lose on an average about 0.005 gram in weight when 200 cc of boiling 1.25 per cent alkali are filtered through them and then washed with hot water until free from alkali. This treatment was tried on four papers, and about the same loss in weight occurred in each case, which indicates that there is a slight error produced in the fiber determination by filtering through paper."

Mr. Sindall prefers Method I. He found difficulties in Method II in removing the hardened material from the dish and also by caking during grinding in the mill, due to the oil. Method III offered no difficulties.

Mr. Smith found filtration through paper extremely unsatisfactory. He made all filtrations on linen, finally washing the fiber into a large dish.

DISCUSSION OF RESULTS.

The agreement on solids in the original indicates that the material was well mixed and that sampling is not difficult. The vagaries of the ether extract results will not be discussed here except to suggest that physical condition and degree of dryness must have some influence on the extraction. On crude fiber the agreement between the analysts is not nearly so good as could be wished and shows that the personal factor is of more consequence than differences in the methods. This is evident from the fact that the individual analysts generally run consistently above or below the general average in all the methods and not in a single method. However, because of this consistency of results, the average for each method should show its relative tendency to give high or low values, although these averages can have little or no significance as to the true or probable value for the sample. In fact the lower values are doubtless nearer the actual truth, since all the difficulties inherent in the methods, such as the effect of the oil in preventing free attack by the reagents, or persistence of any oil in the fiber in Method I, or the hard nature of the residue, or difficulty in grinding sufficiently fine, or loss of oil on the utensils used in preparing the sample in Method II, would all tend to throw results high rather than low. It thus appears from the averages on the dry basis that Method II tends to give the highest and hence probably the most inaccurate results of the three methods. In the opinion of the referee this fact alone, besides the difficulties in grinding the hard and oily sample to uniform fineness and the labor involved, more than offsets the real advantage of a small factor in calculating to a basis for comparison, and makes further experiment with this method inadvisable.

It might be expected that Method III, by reason of previous removal of oil, and also good mechanical condition, would give the lowest results. Such, indeed, appears to be the case, but the average is only slightly below that of

the official method. In fact the results of Method III seem hardly to justify the extra labor involved, and the official method is practically as good, besides being simpler.

Undoubtedly the greatest chances for error in the official method are failure to break up all lumps thoroughly and insufficient washing with water, alcohol, and ether in the last of the process. Altogether, the official method seems to be about the best at present available, but it would seem advisable to strengthen confidence in it by submission to collaborators of samples of prepared mustard of known composition, if possible.

RECOMMENDATIONS.

It is recommended—

(1) That further study be made of the ether extract of paprika, particularly of the index of refraction, with a view to detecting added foreign oils.

(2) That samples of prepared mustard of known composition be submitted to collaborators for the determination of crude fiber by the present official methods.

INDEX OF REFRACTION OF THE ETHER EXTRACT OF PAPRIKA AND PIMENTON.

By D. L. WEATHERHEAD.

At the last meeting of the Association of Official Agricultural Chemists a new method of obtaining the ether extract of paprika was adopted provisionally, and it was suggested that it would be of interest to obtain data on the refractive index of this extract to see if it would be a useful factor in indicating the presence of added oil.

Following this suggestion some data of this nature were collected. No special time was given to the work, but it was done in connection with routine analyses on commercial samples examined at the New York Food and Drug Inspection Laboratory of the Bureau of Chemistry. It is believed, however, that this work throws some light upon the value of the refractive index of the ether extract in indicating the presence of added oil.

The extracts were prepared from the 150 cc of ether solution remaining in the 250-cc flask after the removal of 100 cc for the determination of the amount and iodine number of the extract. The ether solution was filtered into an Erlenmeyer flask and the ether distilled off as in the regular method. The extract was dried in a water oven for half an hour and the refractive index taken at 40° C. in an Abbe refractometer. In all operations the same method of handling and the same precautions were observed as are given for the ether extract in the accepted method. Since it is customary to recover the anhydrous ether from the 150 cc of solution remaining after removal of the portion used in determining the extract, very little extra work is required to obtain the refractive index in the regular course of analysis.

One special precaution seems necessary in reading the refractive index. The entire field is red, one portion being dark red and the balance light red. The border of the dark zone which must be brought on a line with the intersection of the cross hairs shows no dispersion, but upon moving the screw of the compensator attached to the Abbe refractometer the border of the dark zone is seen to move up or down according to the direction in which the compensator is rotated. Only the position and not the distinctness of the border seems to be altered in this way. In order to make the readings in a uniform and comparable way the compensator was always set to give the lowest reading.

In some cases the extracts were allowed to stand for some time before filtering from the residue and also before reading, but the results obtained in these cases do not indicate that the factor is appreciably influenced thereby. So,

although the method outlined is considered preferable, some latitude may be permitted in the details of preparing the extract for the refractive index which could not be permitted in determining the amount and iodine number of the extract.

After taking the refractive index the extracts were set aside in loosely-stoppered flasks and the reading again taken one to two months later, the second reading being in almost all cases practically the same as the first. After standing for nine months under these conditions many of the extracts solidified and became colorless.

As a summary of the indications furnished by the refractive index the following values have been taken from the detailed data obtained:

Extreme and average data on refractive indices of ether extracts of pure and adulterated paprika and pimenton (reading at 40° C.).

Data.	Paprika.		Pimenton.	
	Pure.	With added oil.	Pure.	With added oil.
Minimum.....	1.4720	1.4640	1.4678	1.4660
Maximum.....	1.4825	1.4658	1.4765	¹ 1.4780
Average.....	1.4766	1.4649	1.4725	1.4696
Number of samples.....	25	2	² 16	10

¹ Other factors in the analysis indicate that very little oil could have been used in this sample.

² One sample repeated.

In general the refractive index varies less upon the addition of oil than do the ether extract and iodine number of the ether extract, but on the other hand, it also varies less among samples to which foreign oil has not been added. It appears, therefore, that this new factor can be of use in determining the presence of added oil, and though it can not be considered as conclusive evidence by itself, when taken in connection with the amount of ether extract and the iodine number of the ether extract it is to be regarded as a factor of considerable value.

REPORT ON FATS AND OILS.

By H. S. BAILEY, *Associate referee.*

COLLABORATIVE WORK ON THE DETECTION OF BEEF FAT IN LARD.

The work undertaken this year has been along the lines of the detection of small amounts of added beef fat in lard, by means of the glycerids crystallized from ether solutions. Previous work with the Belfield test,¹ which is now provisional, has indicated that, except in the hands of those who have had considerable experience, it is unsatisfactory for the detection of small amounts of the adulterant.

In 1908 J. E. Emery proposed the substitution of the determination of the melting point of the glycerid crystals in place of their microscopic appearance, as a method for detecting the presence of beef fat.² In the hope that this latter method would be found more satisfactory than the Belfield test, the following samples and directions were sent to 15 collaborators:

Sample No. 15, lard + 3 per cent beef tallow.

Sample No. 16, lard + 5 per cent beef tallow.

¹ U. S. Dept. Agr., Bureau of Chemistry Bul. 107, Rev., p. 147.

² U. S. Dept. Agr., Bureau of Animal Industry Cir. 132.

- Sample No. 17, lard + 10 per cent beef tallow.
 Sample No. 18, lard + 10 per cent lard stearin.
 Sample No. 19, pure lard.
 Sample No. 20, lard + 5 per cent oleo.

DIRECTIONS.

Technique of the method.—Weigh 5 grams of warm, filtered fat, within 0.1 gram, into a glass-stoppered 25 cc cylinder which should be about 18 mm inside diameter. Add warm ether up to the 25 cc graduation, stopper, shake vigorously until solution is complete, then allow cylinder and contents to stand at a temperature of about 18° C. for 18 hours. A slight variation in temperature makes no difference in the results; but the control, which should be run with pure lard each time a doubtful sample is to be tested, must, of course, be crystallized at the same temperature as the sample in question.

After standing the 18 hours, more or less, decant the supernatant ether from the crystallized glycerids, which will usually be found in a compact mass at the bottom of the vessel. Then add 5 cc of cold ether to the crystals in the cylinder, care being taken not to break up the deposit, and decant. This is repeated three times. The last time the crystals should be loosened from the cylinder and transferred to a small filter paper. Wash the crystals with successive small portions of cold ether until 15 to 20 cc have been used, then by means of suction remove the residual ether quickly and transfer the filter paper with its crystals, after having broken up any large lumps of glycerids by gentle pressure, to a desiccator, where they will dry quickly.

The melting point of these glycerids should be determined in an apparatus similar to that indicated on page 134 of Bulletin 107, Revised. The large test tube is approximately 150 by 25 mm and should be about half filled with water. The bulb of the thermometer, with a melting point tube having an internal diameter of about 1 mm, sealed at one end, containing the crystals, is immersed in the water. The test tube is then placed by a beaker of water, care being taken that the surface of the liquid in both test tube and beaker is about the same level. Heat the water in the beaker rapidly to 55° C. and maintain it there until the thermometer carrying the melting-point tube registers a little above 50°. Raise the heat again until the temperature of the outer bath is about 67° C., then remove the lamp and note the temperature at which the glycerids melt to give a perfectly clear transparent liquid. The amount of crystals used for each determination should be approximately the same each time and ought to occupy a space about 9 mm long and be suspended directly opposite the bulb of the thermometer.

In performing this method great care must be exercised in the preparation of the sample. The presence of water and small particles of extraneous matter or the incomplete solution of the fat in the ether may interfere with the process of crystallization, making it too rapid, so that a large mass of small, fluffy crystals, instead of a compact mass of larger ones, as desired, is obtained. The temperature of crystallization should not be less than 15° C. or more than 20°.

Suggestions to collaborators.—It is suggested that collaborators make mixtures of, say, 3, 5, 10, and 20 per cent of these adulterants with the pure lard and from a determination of the melting point of the mixed glycerids in comparison with those obtained from the pure lard, state what, in their opinion, is the minimum amount of each foreign fat that can be detected by the Emery method; also what is the limit with the Belfield test, and, of course, which of the unknowns are pure lards and which adulterated.

The referee will be glad to receive such suggestions and modifications in regard to these methods as seem desirable; but in order to give them, as they stand, a fair test, it will be necessary to carry through one set of determinations exactly as directed. It will also be of value if other samples of lards of known purity be submitted to these tests by collaborators who are in a position to secure such.

TABULATED RESULTS.

Very few results having been received by August 9 and several of the collaborators having indicated that the amount of time which they would be able to give to the work was limited, a further letter was sent out suggesting that

if there were not time for all the work originally outlined, the Emery method only should be tested on the unknown samples. In reply to this the following results were received:

TABLE 1.—*Melting points of glycerids.*

Collaborator.	Sample No. —						Lard.	Tallow.	Lard stearin.	Oleo stearin.
	15	16	17	18	19	20				
R. H. Kerr.....	63.6	63.4	62.8	64.0	64.2	62.2	63.6	59.2	63.8	60.0
R. R. Henly.....	63.4	63.2	62.6	63.9	63.8	62.0	63.6	59.2	63.8	60.0
R. C. Kent.....	64.6	64.6	63.8	64.9	65.0	63.4	64.8	59.6	63.8	59.8
C. P. Wilson.....	63.0	62.6	62.4	63.0	63.6	61.8	63.6	58.6	62.8	59.2
H. S. Bailey.....	63.8	63.6	63.0	64.0	64.1	63.1	64.2	59.2	63.8	60.0
C. W. Harrison.....	63.7	63.6	63.7	64.0	63.6	62.6	64.2	59.2	63.8	60.0
H. D. Poore.....	63.8	63.8	63.1	64.0	64.3	63.1	63.8	60.5	63.9	60.7
W. B. Smith.....	63.7	63.2	63.0	64.1	64.1	62.5	63.9	59.3	63.7	59.2
L. B. Burnet.....	64.0	64.1	63.2	64.2	64.2	63.0	64.1	59.2	63.3	60.0
B. B. Schneider.....	62.8	62.7	61.8	63.2	62.8	61.9	63.6	59.2	63.3	60.0

TABLE 2.—*Differences between pure lard and sample.*

Collaborator.	Sample No. —						Tallow.	Lard stearin.	Oleo stearin.
	15	16	17	18	19	20			
B. B. Schneider.....	-0.8	-0.9	¹ -1.8	-0.4	-0.8	-1.7	-4.4	-0.3
R. H. Kerr.....	.0	-.2	-.8	+ .4	-.6	-1.4	-4.4	+ .2	-3.6
R. R. Henly ²	-.4	-.6	-1.2	+ .1	-1.8
R. C. Kent.....	-.2	-.2	-1.0	¹ +1.2	-1.4	-5.2	-5.0
C. P. Wilson.....	-.6	-1.0	-1.2	-.6	.0	-1.8	-5.0	-.8	-4.4
H. S. Bailey ²	-.3	-.5	-1.1	-.1	-1.0
C. W. Harrison.....	-.5	-.6	-.5	-.2	-.6	-1.6
H. D. Poore.....	.0	-.0	-.7	+ .2	-.5	-.7	-3.3	+ .1	-2.9
W. B. Smith.....	-.7	-.9	+ .2	+ .2	-1.4	-3.6	-.2	-3.7
L. B. Burnet.....	-.1	.0	-.9	+ .1	+ .1	-1.1
Average.....	-.32	-.47	-.92	-.04	-.22	-1.39

¹ Omitted from average.

² Unknown No. 19, which was same as lard sent out taken for calculating difference.

TABLE 3.—*Results showing judgment of collaborators on purity of samples.*

Analyst.	No. 15. 3 per cent tallow.	No. 16. 5 per cent tallow.	No. 17. 10 per cent tallow.	No. 18. 10 per cent lard stearin.	No. 19. Pure lard.	No. 20. 5 per cent oleo.
R. H. Kerr.....	Pure.....	Small adulteration.	4 or 5 per cent.	Pure.....	Pure.....	L a r g e amount.
R. R. Henly.....do.....	Adulterated.	More adulteration.do.....do.....	Adulterated.
R. C. Kent.....	Doubtful.....	Doubtful.....	Adulterated.do.....do.....	Do.
C. P. Wilson.....	Adulterated ¹	Adulterated ¹	Adulterated ¹do ¹do ¹	Do. ¹
.....do.....do.....do.....do.....	Adulterated.do.....	Do.
L. B. Burnet ²	Pure.....	Pure.....do.....	Pure.....do.....	Do.
H. S. Bailey.....	Doubtful.....	Adulterated.do.....do.....do.....	Do.
C. W. Harrison.....do.....do.....	Doubtful.....	Pure.....	Adulterated.	Do.
H. D. Poore ²	Pure.....	Pure.....	Adulterated.do.....	Pure.....	Do.
A. F. Seeker.....	Adulterated ¹do ¹do ¹	Adulterated ¹	Adulterated ¹	Do. ¹
W. B. Smith.....do.....	Adulterated.do.....	Pure.....	Pure.....	Do.
Do.....do.....do.....do.....do.....do.....	Adulterated.
B. B. Schneider...	Adulterated.do.....do.....do.....	Adulterated.	L a r g e amount.
						Adulterated.

¹ Belfield test.

² Calculated, by referee, on assumption that a difference of -0.2° indicates doubtful purity and that a difference of -0.5° shows undoubted adulteration.

COMMENTS OF COLLABORATORS.

A. F. Seeker, New York Food Inspection Laboratory: An examination of the samples sent by the referee, following the directions given under the Belfield test in Bulletin 107, Revised, showed that the lard and lard stearin crystallized from ether in similar form, while most of the crystals obtained from the oleo-stearin and tallow (which also resembled each other) differed from the first two and could readily be distinguished from them under the microscope. Even in the case of pure lard, however, there were a few crystal groups which could not be distinguished from some of the tufts found in pure oleo stearin, so that upon the examination of mixtures of lard and oleo stearin and of the samples numbered 15 to 20, it was in many cases found impossible to tell with absolute certainty whether the characteristic beef stearin crystals were present or not. I feel that the Belfield test in its present form is unreliable, and report the results obtained without confidence in their accuracy.

Homer D. Poore, New York Food Inspection Laboratory: It was found that the melting point varied directly with the amount of oleo stearin present up to 10 per cent, but the 10, 20, and 40 per cent mixtures gave the same melting point. The melting points obtained with the 3 and 5 per cent mixtures show that a difference of 1 per cent of oleo stearin changes the melting point from 0.2° to 0.3° . Therefore an 8 per cent mixture would probably have the same melting point as a 10 per cent. The conclusions arrived at from these results are that amounts of oleo stearin in lard up to 8 per cent may be detected within 1 per cent, while amounts over 8 per cent will give the same melting point, which shows adulteration but gives no indication of the amount of adulteration. A 10 per cent mixture of tallow gave a melting point which showed no adulteration, while a 20 per cent mixture gave one that did.

Paul Rudnick, Armour & Co.: We did quite a lot of work on both the Emery and Belfield methods, and in addition to that, some by the so-called Stork method; but the results were absolutely unsatisfactory, chiefly because of a lack of facilities for maintaining the correct temperature.

R. H. Kerr, Bureau of Animal Industry: The slight difference noted between Mr. Henley's results and my own are due to a slightly lower temperature of crystallization which he employed. The temperature for my work was between 17° and 18° C.

B. B. Schneider, Bureau of Chemistry: It would be better, in my opinion, if in the determination of the melting points the temperature of the outer bath were held at a maximum of 65° or 66° C. for high melting-point mixtures. When held at 67° C. the rise of temperature of the inner bath is too rapid for accurate reading.

SUMMARY OF RESULTS.

Summarizing in brief the results tabulated in Table 2:

On sample No. 15, which contained 3 per cent of tallow, of the 9 collaborators reporting, 4 were incorrect, 3 doubtful, and 2 correct, in their judgment of the purity.

Similarly with No. 16 containing 5 per cent of added tallow, 11 reports were received of which 2 were wrong, 1 doubtful, and 8 correct.

On sample No. 17, containing 10 per cent of tallow, 11 reports were received, of which none was wrong. 1 was doubtful, and 10 were correct.

On sample No. 18, containing 10 per cent of lard stearin, which while not lard in the true sense is still a hog fat and, therefore, not detectable by either of the methods tried, 11 reports were received, 1 being incorrect, 10 correct.

Sample No. 19, which was the same pure lard as that sent for comparison, was reported by 2 collaborators as adulterated while 8 were correct in their judgment.

Sample No. 20, containing 5 per cent of oleo, was in every case reported as adulterated.

The tabulated results and the comments of various collaborators indicate a wide difference of opinion as to the value of the proposed method. That it can be carried out with much more facility and less expensive apparatus, no microscope being needed, than the Belfield test, there is no doubt, and as it

has been in constant use in the Bureau of Animal Industry for the past two or three years and has given full satisfaction, I think it wise that steps be taken to have it adopted as provisional. Further work, however, should be done on this method next year, and it is hoped that with this year's experience attention can be confined to a narrower field of investigation, so that the time which it will be necessary for collaborators to give to future work will be very small.

REPORT ON THE ADULTERATION OF DAIRY PRODUCTS.

By A. E. PAUL, *Associate Referee.*

At last year's meeting, further study of the Roesse-Gottlieb method, as applied to ice cream, milk powders, malted milk, milk chocolate, and cheese was recommended. This work, however, naturally falls to the referee on dairy products, and there was no recommendation properly coming under the head of adulteration.

Looking over this field, the referee was struck by the possibilities for fraud introduced by the "homogenizer," which is just coming into use. This machine enables the unscrupulous manufacturer not only to substitute process butter and skimmed milk for cream, but to "fill" any or all dairy products with whatever foreign fat he chooses to employ. The difficulty of incorporating such adulterants has, up to the present time, practically prevented such practice.

The study of the examination of fats, unmixed with other ingredients, has been very thoroughly carried on by the referees on that subject. However, the separation of sufficient fat for a suitable examination, from such products as ice cream, condensed milk, evaporated milk, cream and fresh milk, presents certain difficulties. At least 7 to 10 grams are required, and from a given sample, the fat should be separated quantitatively or nearly so, in order to eliminate the possibility of a selective separation of fatty bodies. Any chemical alteration of the fat must be avoided and oxidation must be guarded against.

In working out a suitable method several attempts proved unsatisfactory. One of these, a wet method based upon the Roesse-Gottlieb method, was fairly successful, but had to be discarded because of the large amounts of inflammable materials involved, which would render the operations exceedingly dangerous. The method to be described appears to be in every way satisfactory. The separation of the fat is practically quantitative, the time consumed in carrying out the operation is insignificant, and the amount of volatile solvent used is very small indeed.

Unfortunately, circumstances made it impossible to carry out this work until rather late in the year. The method was submitted to the collaborators with the request that it be tried on samples procured in the open market and a report returned, this to include the determination of fat by the Roesse-Gottlieb method, and the percentage of fat recovered by the method submitted.

Owing no doubt to the lateness of the request, no returns were received. My own results on three products examined were as follows:

Vanilla ice cream:

Fat, Roesse-Gottlieb.....	per cent..	7.58
Fat recovered from 100 grams of sample.....	grams..	7.61

Evaporated milk:

Fat, Roesse-Gottlieb.....	per cent..	7.83
Fat, recovered from 100 grams of sample.....	grams..	7.68

Condensed milk (sweetened):

Fat, Roesse-Gottlieb.....	per cent..	9.03
Fat, recovered from 100 grams of sample.....	grams..	8.95

It is recommended that the method, which reads as follows, be further studied:

Method of extracting fat from cream, ice cream, evaporated milk, and sweetened condensed milk.—Into a 1,000-cc beaker weigh 100 grams (cream, 50 grams) of the material. Add 300 cc water, mix thoroughly, and bring to a boil. Then add, while boiling, very gradually, 25 cc of Soxhlet's copper sulphate solution, diluted with 100 cc water.

In a Büchner funnel wet a filter of suitable size and of loose texture. Filter with suction and wash three times with a little boiling water. Filter as dry as possible. Remove the cake, which should be dry enough to be broken up easily between the fingers. Break into small particles and dry in the open air overnight. Grind in a mortar with a sufficient amount of anhydrous copper sulphate (usually 25 grams is enough) and let stand for a few minutes, or until the product seems quite dry and not at all lumpy.

Put a layer of anhydrous copper sulphate in the inner tube of a large extractor and then add the powdered mixture. Place a loose plug of cotton on top of the mixture and extract with ordinary ether. The ether should be poured into the extractor and allowed to percolate through before the heating is begun. Approximately 50 cc of the solvent will be required. Dry and weigh the fat.

REPORT ON CEREAL PRODUCTS.

By H. L. WHITE, *Associate Referee.*

INTRODUCTION.

At the meeting of this association held in 1910 it was recommended, "That the associate referee on cereal products be instructed to devote special attention to methods for analyzing and testing wheat and flour."

Plan of work.—As no methods for the analysis of cereal products are included under that head in Bulletin 107, Revised, it was deemed advisable by the associate referee to try out, as far as possible, all methods in general use by members of this association and others interested in this line of investigations. Accordingly, after correspondence with several members of the association, methods were collected from various sources and sent, together with two samples of flour, to each of the 10 chemists who offered to collaborate in this work.

Samples.—Sample A was a straight flour from Fife wheat of the 1909 crop, grown in the Red River Valley, near Fargo, N. Dak., and had been in storage in the elevator of the mill at the North Dakota agricultural experiment station until milled March 29, 1911. Sample B was a patent flour from durum wheat, Arnautka variety, of the crop of 1909, grown at Edgeley, N. Dak. The wheat was in storage in the same elevator as sample A until milled March 29, 1911.

METHODS.

The statements in parentheses indicate source or by whom suggested.

MOISTURE.

Method A.—(Adapted from Leach's Food Inspection and Analysis.) Weigh out 5 grams of flour into a flat-bottomed dish, and dry five hours in a water oven at temperature of boiling water.

(NOTE.—Flat-bottomed dishes of aluminum are excellent for use in this method.)

Method B.—(Bul. No. 122, pp. 53-54.) Dry a convenient quantity of flour, approximately 5 grams, at the temperature of boiling water, in a current of dry hydrogen or in vacuo, until it ceases to lose weight.

Method C.—(H. P. Bassett, Bul. No. 122, pp. 55-58.) After treatment with ether (see ether extract, Bassett's method), dry the residue for five hours in a water oven. The loss in weight represents both ether extract and moisture. From total loss in weight per cent subtract the per cent of ether extract.

ASH.

Method A.—(A. L. Winton.) Burn 5 grams of flour in an electric muffle furnace below redness. In case an ash free from carbon is not obtained, add a few drops of nitric acid, evaporate on a water bath, and place again in the muffle furnace for a few moments, repeating the operation two or three times if necessary.

Method B.—(Bul. No. 122, p. 54.) Char a convenient weight of the original sample, approximately 5 grams, in a platinum dish, in a muffle, at the lowest possible temperature until free from carbon. If carbon-free ash can not be obtained owing to its fusibility, cool, add a small quantity of water, warm slightly, drain the more soluble portions of the ash from the carbonaceous residue, carefully dry, and reincinerate to constant weight.

NOTE.—A few drops nitric acid may be added, but if so the ash must be carefully fused until all evolution of gases ceases or slightly high results are likely to be obtained.

Method C.—(Adapted from 2 (b), p. 21, Bul. 107, Revised.) Weigh out 5 grams of flour into a porcelain crucible, moisten thoroughly with 10 cc of calcium acetate solution and dry on a hot plate. Heat over an ordinary burner, with low flame, until ash is white, then use blast lamp one minute, cool and weigh. Subtract weight of calcium oxid from total weight. The calcium acetate solution is made by dissolving 1.8 grams precipitated calcium carbonate in pure acetic acid and diluting to 1 liter. Standardize by evaporating 10 cc of the solution to dryness and treat as an ash.

ETHER EXTRACT.

Method A.—(Bul. No. 122, p. 54.) Extract a convenient quantity of the product (from 4 to 5 grams) as dried in the determination of moisture with anhydrous, alcohol-free ether, for 24 hours (with fine flour the addition of an equal weight of clean, dry sand is frequently necessary). Dry the extract at the temperature of boiling water until it ceases to lose weight.

NOTE.—Iodin numbers should be obtained upon the ether extract after purification by solution in petroleic ether, but are best made upon the petroleum ether extract.

Crude ether extract may also be purified with acetone for the determination of the iodine number.

Method B.—(H. P. Bassett, Bul. No. 122, p. 55.) Weigh 10 grams of flour into a tared Gooch crucible of about 20 grams capacity, place in an ordinary Gooch funnel and insert, by means of a two-hole rubber stopper, into the top of a low bell jar resting on a glass plate. Fill the crucible six times with anhydrous alcohol-free ether, drawing off each portion with a filter pump. Collect the ether extract in a bulb flask similar to those used with a Soxhlet apparatus. Connect the bulb with an upright condenser and distil off the ether, using a 32 candlepower lamp as a source of heat. Dry the flask one hour in the water oven, cool and weigh.

ACIDITY OF WATER EXTRACTS OF FLOUR.

Method A.—(Bul. No. 122, p. 54.) Weigh 18 grams of flour into a 500 cc Erlenmeyer flask and add 200 cc of distilled water previously freed from carbon dioxide by boiling in tin and neutralized if need be. Place loosely stoppered flask in a water bath kept at 40° C. for 10 minutes, shaking repeatedly. Remove the flask and allow it to stand, with occasional shaking, at room temperature for one hour. Filter upon dry folded filter, rejecting the first 10 cc and receiving the succeeding 100 cc in a graduate flask. Titrate the filtrate with twentieth-normal sodium hydroxid, using carefully neutralized phenolphthalein in alcohol as an indicator. Each cubic centimeter of twentieth-normal sodium hydroxid represents 0.05 per cent of acidity as lactic acid.

NOTE.—Results obtained with flour at temperatures of 15°, 20°, and 25°, respectively, indicate that the acidity in the solution increases with the temperature. The method outlined above seems to give the maximum acidity.

Method B.—(H. L. White.) Proceed as in Method A, except that the flask should be kept in a water oven maintained at 40° C. for two hours, shaking vigorously every half hour. At the end of the two-hour period decant the liquid portion, shake with 10 to 20 grams of kaolin or clean quartz sand before pouring on filter paper. Express as per cent lactic acid.

SOLUBLE CARBOHYDRATES AS DEXTROSE.

Method A.—(Bul. No. 122, p. 54.) Weigh 16 grams of flour into a 500 cc flask. Add 200 cc of water. Shake occasionally during one-half hour. Filter through a dry folded filter. To 50 cc of the filtrate add 5 cc of concentrated hydrochloric acid. Place the flask in water and invert at 70° C. for 10 minutes. Cool, neutralize, and bring to 100 cc. Filter. Determine the reducing sugars with Fehling solution, by the official method, as described in Bulletin 107, Revised, calculating the reducing sugars as dextrose.

The methods of A. H. Bryan, A. Given, and M. N. Straughn for the determination of sugars (Bureau of Chemistry Circular No. 71) were also recommended for trial by the collaborators. These methods are stated as follows:

Statement of Bryan, Given, and Straughn method for sugars in cereals, etc.

(a) *Preparation of solution.*—Place 12 grams of the finely ground material in a 300 cc graduated flask, with 1 to 3 grams of precipitated calcium carbonate to neutralize the acidity, add 150 cc of 50 per cent alcohol by volume (carefully neutralized), mix thoroughly, and boil on steam bath for one hour, using a small funnel in the neck of the flask to condense the vapor. Cool, make to volume (300 cc) with 95 per cent alcohol (neutral in reaction), mix thoroughly, allow to settle. Transfer 200 cc to a beaker with a pipette and evaporate on a steam bath to a volume of from 20 to 30 cc, *but not to dryness*. This should remove all but traces of alcohol. Add 20 cc of water, stir, and transfer the solution to a 100 cc graduated flask and wash the beaker with water into the flask. Add to this enough saturated solution of neutral lead acetate from a burette or pipette to produce complete precipitation, but avoid an excess. Allow to stand 15 minutes and make up to volume of 100 cc with water, shake well, and filter. At least 75 cc of filtrate should be obtained. Add anhydrous sodium carbonate or potassium or sodium oxalate to precipitate all the lead, allow to stand 15 minutes, and pour onto an ashless filter. Test the filtrate for lead with small quantities of the precipitating agents mentioned above and refilter if necessary. This solution represents the sugars from 8 grams of the original material and is used in the following determination:

(b) *Reducing sugars.*—Twenty-five cubic centimeters of the filtrate, together with 25 cc of water, are used as the sugar solution for Munson and Walker's method (see p. 241, Bul. 107, Rev.), or 25 cc of the solution can be used for Allihn's method (see p. 49, *ibid.*). With Allihn's method the amount of dextrose found is multiplied by the factor 1.044 to obtain the equivalent in invert sugar.

(c) *Sucrose.*—In a covered 400 cc beaker place 50 cc of the filtrate from (a). In case sodium carbonate was used to throw out the lead, add a small piece of litmus paper or neutralize with acetic acid, then add 5 cc of concentrated hydrochloric acid and allow to stand overnight for inversion. Where potassium or sodium oxalate was used for removing lead it is not necessary to neutralize, but the acid can be used direct. At the expiration of the 24 hours neutralize with anhydrous sodium carbonate and wash into a 100 cc flask and make up to the mark. Filter if necessary, and use 50 cc for the determination of total sugars as invert by the method of Munson and Walker or 25 cc by the method of Allihn. The percentage of reducing sugars before inversion calculated as invert sugar is subtracted from the percentage of total invert sugar after inversion, and this product multiplied by 0.95 gives the percentage of sucrose.

For more exact results it is necessary to determine the volume occupied by the 12 grams of material used in this work and to account for it. A large number of determinations have shown the average volume of 12 grams to be 9 cc. Therefore the correction for this would be 0.97, and hence the percentage of original sugars and sucrose should be multiplied by this factor to obtain the true amounts.

GASOLINE COLOR VALUE.

Method A.—(A. L. Winton, see Bul. 137, p. 146, for full statement of method.)

NOTE.—A. S. Mitchell recommends the use of a Kennicott-Sargent colorimeter, using a 0.005 per cent water solution of potassium chromate as a standard.

TOTAL NITROGEN.

Method A.—(Bul. No. 122, p. 54.) Determine the total nitrogen in 2 grams of flour according to the official method, preferably the Gunning method. Bulletin 107, Revised, page 7. The nitrogen times 5.75 gives total $\frac{1}{2}$ proteids.

ALCOHOL SOLUBLE PROTEIDS.

Method A.—(Bul. No. 122, p. 55.) Weigh 4 grams of flour into a 500 cc Erlenmeyer flask, add 200 cc of alcohol, 0.90 specific gravity. Shake occasionally during three hours. Let stand twelve hours. Filter through a dried filter. Evaporate the alcohol from 100 cc of the filtrate after the addition of 5 cc of sulphuric acid and determine the nitrogen as alcohol soluble nitrogen. (This figure less the amid nitrogen gives the alcohol soluble proteid nitrogen or gliadin.)

GLOBULIN AND ALBUMEN (EDESTIN AND LEUCOSIN) AND AMID NITROGEN.

Method A.—(Bul. 122, p. 54.) Weigh 5 grams of flour into a 500 cc Erlenmeyer flask. Add 250 cc of sodium chlorid solution 1 per cent. Stopper and shake thoroughly. Let stand, with occasional shaking, for three hours. Filter on dry paper. Evaporate 100 cc of the filtrate to small volume in a Kjeldahl digestion flask with 5 cc of sulphuric acid. Add remainder of the sulphuric acid and determine the nitrogen by the Gunning method. To a second 100 cc of the filtrate add 5 cc of phosphotungstic acid, 20 per cent solution; shake thoroughly, allow to settle, and filter by decantation. Wash slightly with water. Concentrate the filtrate with 5 cc of sulphuric acid in Kjeldahl flask and determine the nitrogen as amid.

Deduct the amid nitrogen from the nitrogen found in the first fraction to obtain the nitrogen as globulin and albumen. This figure times 6.25 gives globulin and albumen.

GLUTENIN (BY DIFFERENCE).

Method A.—(Bul. No. 122, p. 55.) Deduct from the total nitrogen the salt soluble nitrogen plus the gliadin. This times 6.25 gives the glutenin.

GLIADIN BY POLARIZATION.

Method A.—(Snyder, Bul. No. 122, p. 55.) Weigh 15.97 grams of flour into a 300 cc flask. Add 100 cc of 0.90 specific gravity alcohol. Shake at intervals during three hours and let stand overnight. Filter through a dry folded filter. Polarize in a 220 mm tube. Precipitate the proteids in 50 cc of the filtrate with 5 cc of Millon's reagent. Shake, filter, and polarize the filtrate in a 220 mm tube. Add 50 per cent to the reading and deduct the sum from the first reading. This difference times 0.2 gives the per cent of nitrogen as gliadin.

Method B.—(D. W. Shaw.) Weigh 15.97 grams of flour into a 300 cc flask, add 100 cc of 0.90 specific gravity alcohol. Shake at intervals during three hours and let stand overnight. Filter through a dry folded filter. Polarize in a 200 mm tube. Precipitate the proteids in 50 cc of the filtrate with 5 cc of Millon's reagent. Shake, filter, and polarize the filtrate in a 200 mm tube. Add 10 per cent to the reading and deduct the sum from the first reading. This difference times 0.2 gives the per cent of nitrogen as gliadin.

(NOTE BY A. S. MITCHELL.—Fleurent has devised a modification for gliadin in which an addition of 0.2 per cent of sodium hydroxid is added to the 70 per cent alcohol. In our trials thus far the mixture has been hard to filter, and the modification has not proved very satisfactory. Please also note that various workers are using slightly different percentages of alcohol; for example, Shaw has used specific gravity 0.90. Many workers use 70 per cent by volume. It seems immaterial to me which is used, but I think one or the other ought to be definitely fixed upon.)

DETERMINATION OF MOIST GLUTEN.

Method A.—(Bul. No. 122, p. 54.) Dough up 30 grams of flour with 18 cc of water conveniently in an 8-ounce mortar. Weigh off 16 grams of dough equivalent to 10 grams of flour. Place in water at room temperature for one

hour and carefully wash out the starch over boiling cloth or a fine horse-hair sieve. After expressing all globules of water, weigh the moist gluten upon a watch glass. Dry in a desiccator for 24 hours and complete drying in water oven.

CRUDE FIBER.

Method A.—(Bul. No. 122, p. 54.) Determine the crude fiber in 2 grams of flour by the official method (Bul. 107, Rev., p. 56), filtering through linen in a Büchner funnel.

Baking test method (C. H. Bailey).

Formula: Flour, 340 grams; sugar, 15 grams; yeast, 10 grams; salt, 5 grams, and sufficient water.

Method: All ingredients should first be warmed to a temperature of 32° C., and the fermentation conducted in a regulated fermentation cabinet at the same temperature. Weigh 340 grams of flour into a tight can or box, and place in the fermentation cabinet for at least one hour before mixing. The salt may be weighed into one-half gallon stoneware jars, which are used as receptacles for the dough during the fermentation period, and the sugar weighed into packages which are then ready for use at the proper time. The yeast mixture is prepared as follows: Weigh enough compressed yeast for a baking, plus enough for an extra loaf, into a salt-mouth bottle, and add a quantity of warm, distilled water, equivalent to 30 cc for every 10 grams of yeast taken, and mix the whole thoroughly. This mixture should be prepared at least half an hour before the work of sponging is commenced, being allowed to stand in the fermentation cabinet during the interval; 37.6 cc of this yeast suspension is equivalent to 10 grams of yeast and 30 cc of water, and this quantity is taken in mixing each sponge.

The method of incorporating the materials into the dough is as follows: 140 cc of distilled water (or less if the flour is soft and fluffy in character) and 37.6 cc of the yeast suspension are placed in a stoneware jar, which already contains 5 grams of salt, and into this mixture about two-thirds of the flour, or enough to form a soft sponge, is stirred. The jar is covered, placed in the fermentation cabinet, and allowed to remain there for about 90 minutes.

The sponge is then cut out of the jar and placed in a mixing machine (or on a smooth mixing board, provided no machine is available) together with 15 grams of sugar and the remainder of the flour, which has been kept warm in the meantime. When the Werner-Pfleiderer machine is used, about 200 revolutions of the slow blade are required to thoroughly mix the dough. If the mixing is done on a board, it will require from 12 to 15 minutes hand-mixing to produce a dough of uniform consistency. Water is added a little at a time during the mixing until the dough is of the proper consistency. Judging of the consistency is a matter that requires experience and practice, there being no known device that will determine when the proper condition is reached better than the skilled human hand. When thoroughly mixed the dough is returned to the same jar and again placed in the fermentation cabinet for about 45 minutes, at which time it is removed from the jar and the mass of dough lightly molded and replaced the other side up. In about 20 minutes the dough is again removed from the jar, molded into a loaf, and placed in a well-greased, oblong, black, iron baking pan. This pan is 5½ inches deep, 3 by 5½ inches at the bottom, and 3½ by 6½ inches at the top. The mass of dough is pricked about 10 times with a long needle, placed in the fermentation cabinet, and allowed to rise to nearly the maximum. The time of final rising in the pan varies considerably, but it has been found that hard spring wheat patents and straights usually require from 80 to 100 minutes. All the fermentation periods stated must be varied to suit the flour worked with, and also, to a certain extent, the character and condition of the yeast. Elastic doughs made from flours high in gluten of good quality require a longer fermentation period than do doughs made from flours low in gluten. The figures stated are about the average of the periods allowed hard spring wheat straight flours.

When the dough has reached about the maximum volume it will attain, the pan is placed in the oven, which has been previously heated to 175° C. The temperature should be allowed to rise gradually until at the end of about 5 to 8 minutes it has reached a temperature of from 195° to 200° C. Or, two ovens may be used, one being maintained at about 175° C. and the other at about

200° C., and the loaf transferred to the hotter oven at the end of about 5 minutes, at which time it will have attained its maximum volume. The purpose of employing a lower temperature at the outset is to allow the mass of dough to rise or expand all it will in the oven before the temperature becomes high enough to sear or crust over the outside of the loaf, thus preventing further expansion. The total time of baking varies from about 25 to 45 minutes, depending upon the size of the loaf. Small loaves require more time for thorough baking than do loaves of larger volume.

Since certain factors other than temperature, particularly the quality of the yeast used, influence the volume and quality of bread produced from a given flour, a check loaf should be baked each day from the same check lot of flour, and when there is any marked variation from the average results previously secured in working with this check flour, all tests made at the time should be rejected. When the variation from the average is slight, it is deemed permissible to increase or decrease the recorded volume of other loaves in the same baking, in proportion to the variation of the check loaf from the average.

Recording results: In judging of the baking qualities of the flour, the following factors are of principal importance:

(1) The elasticity or expansibility of the dough, as evidenced by the volume of the loaf.

(2) The color of the flour and of the crumb of the bread produced therefrom.

(3) The "absorption" or quantity of water required to produce a dough of proper consistency.

(4) Other factors, such as flavor, odor, etc.

The absorption is determined during the operation of mixing by noting the quantity of water in cubic centimeters required to produce a dough of the proper consistency. The water used is ordinarily stated in the number of cubic centimeters per 100 grams of flour. This, of course, includes water in the yeast mixture which is added and which is considered as being equivalent to 30 cc.

The volume of the loaf is ascertained by displacement of a suitable material, flaxseed being most convenient for this purpose. The cooled loaf is placed in a box of known volume and the remaining space filled with flaxseed, which is then drawn off into a suitable device and measured. The volume may be stated in cubic centimeters of bread produced from 340 grams of flour or cubic centimeters per 100 grams of flour. The American Society of Milling and Baking Technology also recommend that the volume of bread from 100 grams of dry matter also be recorded.

Color is best judged in the crumb of the finished loaf. In this laboratory the color is expressed on an empirical scale ranging from 50 to 100 or above. The whiter the color the higher the color score, dark flours scoring lower, depending upon the depth of color. A good high-grade patent should score 97 or above on this scale; straight flours 94 or above. The lower or clear flour grades score from 90 on down, depending on their quality and character. It is extremely difficult to convey an idea of the way in which these colors are graded in this laboratory without the use of flour samples whose color score has been determined.

The weight of the finished loaf is also recorded, although this factor is not of so much importance as the quantity of water used per unit of flour. This is true because the weight of the finished loaf is influenced not only by the amount of water used but by the size or volume of the loaf as well. Two doughs to which the same amount of water has been added, but which are raised to different volumes, yield loaves the larger of which will be the lighter. It has been found in working with a large number of samples that the quantity of water used furnishes a better indication of the relative weight of bread which may be produced from a given unit of flour than does the weight of the finished loaf.

Additional remarks concerning abnormalities, such as peculiar odors, flavors, or the like, are included in the report when it is considered necessary. Remarks concerning the crumb texture may also be made, although it is questionable whether this means very much, since the crumb quality may be more nearly a measure of the skill of the operator than of the bread-making qualities of the flour from which it is made. When the dough is sufficiently elastic to produce a loaf of large volume, bread of good quality as regards crumb texture may be produced therefrom in a commercial way.

RESULTS OF ANALYSES.

MOISTURE.

Comparative results obtained by different methods for determining moisture in flour.

Analyst.	Sample A (Fife).			Sample B (durum).		
	Method A (water oven).	Method B (vac- uum).	Method C (Bas- sett's).	Method A (water oven).	Method B (vac- uum).	Method C (Bas- sett's).
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
Leila Dunton, Manhattan, Kans.....	11.01	11.90	11.55	10.52	11.365	11.145
B. R. Jacobs, Washington, D. C.....		¹ 11.72			¹ 11.12	
L. M. Thomas, Agricultural College, N. Dak.....	10.13		10.07	9.54		9.65
R. F. Beard, Agricultural College, N. Dak..	³ 10.32 10.91	² 11.88	10.09	³ 9.94 10.91	11.64	9.88
C. K. Glycart, St. Paul, Minn.....	10.24	11.89	9.97	9.55	11.06	9.35
H. L. White, Agricultural College, N. Dak.	³ 10.50 10.18	10.56	10.595	³ 10.43 9.65	² 10.42	10.53
G. A. Olson, Pullman, Wash.....	⁴ 7.49			⁴ 6.34		
Averages.....	10.47	11.59	10.455	10.076	11.18	10.109

¹ "Drying in a vacuum 4½ hours."

² In vacuum oven at 70° C. for periods ranging from 24 to 144 hours.

³ In aluminum dishes fitted with covers.

⁴ Kept in water oven at boiling temperature for 3 hours; not included in average.

Miss Leila Dunton says: "Moisture Method A we do not use in this laboratory for flour samples as it fails to remove all moisture. Method B is very good. The vacuum desiccator we find very convenient and accurate."

These results strengthen the conviction that for accurate results, when working with materials that are affected by the temperature of boiling water, the method utilizing the vacuum oven or desiccator is the most accurate; but this method should be standardized as regards temperature and other conditions. As indicated in the footnotes to the preceding table the time varied from 4½ hours to 144 hours, and the temperature from room temperature to 70° C.

Method C (Bassett's) may well be considered further as a quick method for the approximate determination of both moisture and fat.

ASH.

Comparative results obtained by different methods for the determination of ash in flour.

Analyst.	Sample A (Fife).			Sample B (durum).		
	Method A (electric muffle).	Method B (muffle furnace).	Method C (addition calcium acetate).	Method A (electric muffle).	Method B (muffle furnace).	Method C (addition calcium acetate).
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
Leila Dunton, Manhattan, Kans.....		0.708	0.706		0.69	0.688
L. M. Thomas, Agricultural College, N. Dak.....			.647			.702
H. L. Wessling, Chicago, Ill.....	0.72			³ 0.69 .70		
B. R. Jacobs, Washington, D. C.....	.70			.69		
R. F. Beard, Agricultural College, N. Dak..			.695			.70
H. L. White, Agricultural College, N. Dak.	.71			.718		
C. K. Glycart, St. Paul, Minn.....	.678	.673	.663	.686	.673	.661
Averages.....	.702	.69	.678	.697	.681	.688

Miss Leila Dunton says: "Ash Method B gives very satisfactory results, but requires much more careful handling than the calcium acetate method."

A. S. Mitchell writes: "Referring to the ash determination by Method C, if the results in this laboratory are confirmed by those of other experimenters, it would seem to indicate that the addition of a lime salt, instead of increasing the ash content by the fixation of organic phosphorus and sulphur, has resulted in the loss of alkalis by the use of a temperature far above the point of volatilization of potash.

"The results indicate that the use of a muffle furnace is necessary for the most accurate results. Since Methods A and B give practically the same results, there seems to be no necessity for distinguishing between a method in which an ordinary muffle is used and one where an electric muffle is employed.

"In handling a large number of samples, the calcium acetate method (Method C) is very convenient and may well be retained as a provisional method."

ACIDITY OF WATER EXTRACT.

Comparative results obtained by different methods for the determination of the acidity of water extracts of flour.

Analyst.	Sample A.			Sample B.		
	Method A (lactic acid).	Method B (lactic acid).	Other methods (lactic acid).	Method A (lactic acid).	Method B (lactic acid).	Other methods (lactic acid).
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
Leila Dunton, Manhattan, Kans.....	0.29	0.31		0.26	0.29	
B. R. Jacobs, Washington, D. C.....	.275			.265		
H. L. Wessling, Chicago, Ill.....			¹ 0.212			¹ 0.185
A. L. Winton, Chicago, Ill.....			1, 212			1, 180
R. F. Beard, Agricultural College, N. Dak..	.258	.268		.210	.225	
L. M. Thomas, Agricultural College, N. Dak.	.198	.204		.218	.222	
C. K. Glycart, St. Paul, Minn.....	.246	.287		.196	.254	
Averages.....	.253	.267	.212	.230	.248	.183

¹ Method found in Leach's Food Inspection and Analysis, 2d ed., p. 320.

The following comments were made by analysts:

A. L. Winton: I would like to see a careful study made of the effects of temperature, different times of shaking, relative volume of flour and water on the percentage of acidity. Our method has always been to shake 20 grams of flour for 5 minutes with 200 cc of water, allow to stand for a half-hour, filter, and titrate. This work has been done at room temperature and the solution obtained has been for determination of nitrous nitrogen as well as for acidity. As a matter of convenience, I would like to see a method finally adopted which would combine both determinations, that is, that the aliquots from the same solution could be used for determining both nitrous nitrogen and acidity.

Miss Dunton: Acidity Method A seems to me impractical on account of the varying room temperature, and the temperature playing so important a part in this determination.

A. S. Mitchell: Method B for acidity gives slightly higher results and the results are, if anything, more concordant providing kaolin is not used. The kaolin which we used apparently contributed somewhat to neutralizing the acid. Possibly if it had been previously treated with acid, washed, and dried, its addition would prove desirable, but without this treatment it might become a source of error. It does not seem sufficient to shake the kaolin with water and titrate with acid for a blank. Possibly shaking it with a dilute acid and titrating back might determine the proper correction.

There is a slight increase in acidity by Method B in every case where the collaborator has reported results by both Methods A and B; and it would seem that this method should be given further trial particularly with reference to the action of kaolin, or even as to the necessity of its use, as is suggested in the comment of A. S. Mitchell.

ETHER EXTRACT.

Comparative results obtained by different methods for determination of the ether extracts.

Analyst.	Sample A (Fife).		Sample B (durum).	
	Method A (extract 16 hours).	Method B (Bassett's).	Method A (extract 16 hours).	Method B (Bassett's).
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
Leila Dunton, Manhattan, Kans.....	1.365	1.30	1.31	1.30
B. R. Jacobs, Washington, D. C.....	1.22		1.35	
L. M. Thomas, Agricultural College, N. Dak.....		1.30		1.25
R. F. Beard, Agricultural College, N. Dak.....		1.38		1.27
H. L. White, Agricultural College, N. Dak.....	¹ 1.67	1.245		1.21
C. K. Glycart, St. Paul, Minn.....	² 1.40	1.27	1.345	1.205
Averages.....	1.414	1.299	1.335	1.247

¹ Flour previously dried in vacuum oven.

² On hydrogen-dried flour.

These results indicate the general superiority of Method A, but the wide variations suggest that some details of the method may be improved. This method is already official for crude fat in foods and feeding stuffs (Bul. 107, Rev., p. 39), but in its application to flour some detail, possibly the manner of determining the moisture in the flour, seriously affects the result. For reasons already stated under "Moisture," Method B (Bassett's) may well be further considered.

SOLUBLE CARBOHYDRATES AS DEXTROSE.

Comparative results obtained by different methods for the determination of soluble carbohydrates in flour.

Analyst.	Sample A (Fife).			Sample B (durum).		
	Method A (Bul. 122).	Extraction with sodium carbonate.	Extraction with alcohol.	Method A (Bul. 122).	Extraction with sodium carbonate.	Extraction with alcohol.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
B. R. Jacobs, Washington, D. C.....	2.38		1.40	2.95		1.78
L. M. Thomas, Agricultural College, N. Dak.....	2.43			2.89		
R. F. Beard, Agricultural College, N. Dak.....	2.365	¹ 2.15	¹ 1.46	2.595	¹ 2.57	¹ 1.918
W. L. Stockham, Agricultural College, N. Dak.....	2.31	¹ 1.90	¹ 1.39	2.83	¹ 2.21	¹ 1.80
Averages.....	2.37	2.03	1.42	2.816	2.39	1.83

¹ Method of Bryan et al., Cir. 71.

These results with alcohol extraction are in quite close agreement, and should be given further trial.

GASOLINE-COLOR VALUE.

Comparative results on Winton's method (a).

Analyst.	Sample A (Fife).	Sample B (durum).
	<i>Per cent.</i>	<i>Per cent.</i>
Leila Dunton, Manhattan, Kans.....	1.225	1.57
H. L. Wessling, Chicago, Ill.....	1.12	1.40
A. L. Winton, Chicago, Ill.....	1.12	1.42
R. F. Beard, Agricultural College, N. Dak.....	1.30	1.49
L. M. Thomas, Agricultural College, N. Dak.....	1.24	1.38
Averages.....	1.20	1.45

NITROGEN.

Comparative results on total nitrogen, globulin, and albumen, and amid nitrogen.

Analyst.	Sample A (Fife).				Sample B (durum).			
	Total nitro- gen.	Protein (N×5.75).	Globulin and albumen nitrogen.	Amino nitro- gen.	Total nitro- gen.	Protein (N×5.75).	Globulin and albumen nitrogen.	Amino nitro- gen.
Leila Dunton, Manhattan, Kans.....	<i>Per ct.</i> 2.505	<i>Per ct.</i> 14.4	<i>Per ct.</i> 10.502	<i>Per ct.</i> 0.082	<i>Per ct.</i> 2.715	<i>Per ct.</i> 15.6	<i>Per ct.</i> 20.507	<i>Per ct.</i> 0.105
W. L. Stockham, Agricul- tural College, N. Dak.....	2.33	-----	-----	-----	2.56	-----	-----	-----
B. R. Jacobs, Washington, D. C.....	2.34	-----	-----	-----	2.53	-----	-----	-----
R. F. Beard, Agricultural College, N. Dak.....	2.34	-----	-----	-----	2.48	-----	-----	-----
G. A. Olson, Pullman, Wash.	2.472	14.21	.503	.073	2.73	15.70	.494	.116

¹ Reported as 2.886 per cent protein.² Reported as 2.916 per cent protein.

The close agreement between three out of five of these determinations of total nitrogen seems sufficient evidence to warrant making the method official.

Results on alcohol-soluble protein obtained by determining nitrogen in solution (Method A).

Analyst.	Sample A (Fife).	Sample B (durum).
	<i>Per cent N.</i>	<i>Per cent N.</i>
Leila Dunton, Manhattan, Kans.....	¹ 1.406	² 1.65
W. L. Stockham, Agricultural College, N. Dak.....	1.31	1.52
B. R. Jacobs, Washington, D. C.....	1.33	1.53
G. A. Olson, Pullman, Wash.....	1.445	1.64
Average.....	1.37	1.53

¹ Reported as 8.085 per cent protein.² Reported as 9.53 per cent protein.

MOIST GLUTEN.

Comparative results obtained by two methods.

Analyst.	Sample A (Fife).				Sample B (Durum).			
	Method A (Bul. 122, p. 54).		Wiley method modified. ¹		Method A (Bul. 122, p. 54).		Wiley method modified. ¹	
	Moist.	Dry.	Moist.	Dry.	Moist.	Dry.	Moist.	Dry.
Miss Leila Dunton, Manhattan, Kans.	<i>Per cent.</i> 33.7	<i>Per cent.</i> 13.1	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i> 35.5	<i>Per cent.</i> 13.3	<i>Per cent.</i>	<i>Per cent.</i>
G. A. Olson, Pull- man, Wash.	-----	-----	37.57	13.815	-----	-----	40.00	15.564

¹ The wet and dry gluten determinations were made according to the Wiley method—with this difference: 10 grams of flour plus 6 cc of water were mixed instead of 30 grams of flour and 18 cc of water. The wet gluten wads were then placed in the vacuum oven and dried for three hours under 65 mm vacuum and 85° C. temperature. Note: The reduced pressure and temperature combined cause the glutens to expand rapidly, and the resulting large surface exposed under these conditions permits the water to be driven off rapidly.

BAKING TESTS.

Comparison of results obtained by different bakers.

Baker and sample.	Weight flour.	Water ab- sorbed.	Fermentation periods.				In pan.	Weight loaf.	Vol- ume.	Color.	Tex- ture.
			1	2	3	4					
Sample A (Fife):											
L. M. Thomas, Agri- cultural College, N. Dak.	<i>Grams.</i> 340	<i>cc.</i> 196	<i>Min.</i> 81	<i>Min.</i> -----	<i>Min.</i> 40	<i>Min.</i> 25	72	<i>Grams.</i> 490	<i>cc.</i> 2,490	98	98
C. H. Bailey, Agri- cultural College, N. Dak.	340	177	-----	-----	-----	-----	-----	483	2,520	101	99
Leila Dunton, Man- hattan, Kans.	340	192	-----	-----	-----	-----	-----	473	1,990	1 96	1 90
B. R. Jacobs, Wash- ington, D. C.	2 300	205	90	3 60	47	20	65	485	2,135	90	100
Sample B (durum):											
L. M. Thomas, Agri- cultural College, N. Dak.	340	205	90	-----	40	25	86	495	2,160	98	97
C. H. Bailey, Agri- cultural College, N. Dak.	340	186	-----	-----	-----	-----	-----	494	2,020	91	99
Leila Dunton, Man- hattan, Kans.	340	187	-----	-----	-----	-----	-----	468	1,780	1 96	1 85
B. R. Jacobs, Wash- ington, D. C.	2 300	202	90	3 60	45	20	55	488	1,681	95	100
		4 227	-----	-----	-----	-----	-----	515	1,672	95	100

¹ Graded in comparison to a loaf baked at the same time from a straight hard winter-wheat flour, which was graded 100 per cent on both color and texture.

² Dry flour.

³ This fermentation period was not included in the original method.

⁴ Second analysis by method used in Bureau of Chemistry, see following section.

METHODS OF MAKING BAKING TESTS USED IN THE LABORATORY OF PLANT PHYSIOLOGICAL CHEMISTRY, BUREAU OF CHEMISTRY.¹

Ferment.—Mix 80 grams of compressed yeast, 80 grams of sugar, and 40 grams of salt in 1,200 cc of water at 30° C. It is best to dissolve yeast in a small amount of this water and add it to the remaining portion. This liquid is kept in the sponge box at 30° C. for one hour.

Dough.—Place 340 grams of flour, previously warmed in a sponge box to 30° C., in a crock, add 150 cc of the yeast mixture and enough water at 30° to make a dough of the standard consistency. The mixing is done with a knife or a larger spatula and requires but one or two minutes' stirring. Place the

¹ By B. R. Jacobs.

crook containing this dough in the sponge box for 20 minutes, at the end of which time remove it, scrape the dough with a spatula from the sides of the crook and fold over in the hands 21 times, place in the crook and in the sponge box for 20 minutes; take out and fold over 14 times, again place in the crook and in the sponge box for 20 minutes; take out and fold in the same manner 9 times. Place in the crook and sponge box for another 20 minutes, take out and fold once or twice. place in the baking pan, smooth surface up, prick with a long pin 10 or 12 times, and place in the sponge box and raise to the maximum, which requires from 50 to 70 minutes, according to the kind of flour to be tested; then place in the oven, the temperature of which is 210° C., and bake for 40 minutes. The baking tests are run in sets of seven. There is enough ferment in the above-mentioned quantity for eight bakes. If it is desired to bake a second set of loaves another ferment is started about 70 minutes after the first so as to allow sufficient time between the ferments for the manipulating of the dough.

After the bread is baked it is allowed to cool for one hour, weighed, and measured, the measurement being done by displacement in a vessel of known volume, using turnip seed to fill that space in the vessel not occupied by the loaf.

ADDITIONAL BAKING TESTS.

G. A. Olson, of Pullman, Wash., submitted the following method and results obtained therewith:

Method.—The baking tests were made on 100 gram lots of flour, which were worked up with a yeast solution containing the requisite amount of water, sugar, and salt, and placed in 300 cc cubical tins for expansion at 32° C. for straight bakes. A second lot was placed in porcelain dishes, covered with watch glasses and allowed to expand at 32° C. for rekneading. After rekneading these doughs were placed in 300 cc cubical tins and allowed to expand a second time, when finally they were baked at 190° C. for 30 minutes. After a lapse of one hour the loaves were weighed and finally put away in a moist chamber and cut the next morning in order to determine the texture and the color of the crumb. Note: The yeast was developed in potato water containing the requisite amount of sugar, salt, and water. The absorption tests were determined by taking definite amounts of yeast solution and working it up with enough flour to make the proper consistency in each case. The amount of yeast solution required for 100 grams of flour was calculated from the difference in the amount of flour used for the absorption determination from a weighed larger amount of flour.

RESULTS OF BAKING TESTS.

Data.	Sample A.	Sample B.
Straight bake:		
Weight of dough when set in oven to bake (grams).....	162.75	170.75
Weight of loaf (grams).....	138.65	144.20
Volume of loaf (cc).....	350.0	330.0
Approximate specific gravity.....	0.396	0.437
Time for dough to rise (minutes).....	110	110
Number cubic centimeters per pound loaf (calculated).....	1,190	1,122
Shape of loaf.....	Good.	Good.
Texture of crumb.....	Uniform.	Uniform.
Color of crumb.....	Yellow cast.	Yellow cast.
Rekneaded bake:		
Weight of dough when set in oven to bake (grams).....	159.55	147.75
Weight of loaf (grams).....	141.95	142.05
Volume of loaf (cc).....	380.0	360.0
Approximate specific gravity.....	0.373	0.394
Time for dough to rise (minutes)—		
First time.....	110	110
Second time.....	70	70
Shape of loaf.....	Excellent.	Good.
Texture of crumb.....	Slightly open.	Slightly open.
Color of crumb.....	Yellow cast.	Yellow cast.

There is so much variation in methods and results in the baking tests that no very definite conclusions can be drawn. It is highly desirable, however,

that the amounts of the materials used, except water, be the same in all methods. Attention should also be called to the wide variation in moisture content of yeast, sometimes as much as 30 per cent, which, if not taken into account, may affect results considerably.

RECOMMENDATIONS.

It is recommended—

(1) That the method for the determination of moisture stated in Bulletin 107, Revised, page 38 (1), be made official for cereals, and that a further study be made of the efficiency of the vacuum desiccator as compared with the vacuum oven.

(2) That Method B for the determination of ash (Bul. 122, p. 54) be made an official method; and that Method C for the determination of ash (adapted from 2 (b), p. 21, Bul. 107, Rev.) be made a provisional method.

(3) That Method B for the determination of the acidity of the water extract of flour be made a provisional method.

(4) That Method A for the determination of the ether extract (Bul. 107, Rev., p. 39, 5b (1)) be made official.

(5) That the methods of A. H. Bryan, A. Given, and M. N. Straughn (Cir. 71, Bureau of Chemistry), for the determination of soluble carbohydrates, be given a more extended trial.

(6) That Method A for total nitrogen (Bul. 122, p. 54) be made official after making the following change: For "2 grams" read "1 to 2 grams."

(7) That Winton's gasoline color value method be made provisional. (See Bul. 137, p. 146.)

(8) That in further trials of baking methods the amounts of materials used, except water, be the same in all methods; and that the water content of the yeast and the fermenting value of the yeast be given due consideration in all methods.

[The following methods and paper bearing on same were submitted subsequent to the meeting and inserted in the Proceedings in accordance with the motion made by Mr. Winton. (See p. 196.)]

DETERMINATION OF NITROUS NITROGEN.

GRIESS-ILOSVAY METHOD.

(1) *Preparation of reagents.*

(a) *Sulphanilic acid solution.*—Dissolve 0.5 gram of sulphanilic acid in 150 cc of 20 per cent acetic acid.

(b) *Alpha-naphthylamin hydrochlorid solution.*—Dissolve 0.2 gram of the salt in 150 cc of 20 per cent acetic acid with the aid of heat.

(c) *Standard sodium nitrite solution.*—Weigh 0.22 gram of dry C. P. silver nitrite into a 1,000 cc flask, add about 40 cc of hot water and agitate gently until the solution is clear. Add a slight excess of C. P. sodium chlorid, shake until the silver chlorid flocks, make up to 1,000 cc, mix, and allow to settle. Draw off 5 cc of the clear solution and dilute to 1 liter; 1 cc of this solution contains 0.0001 mg of nitrogen as nitrite.

(d) *Standardization of sodium nitrite solution.*—The sodium nitrite solution may be standardized as follows: Make a solution of sodium nitrite similar to that provided in (c), but making the first dilution of five times the concentration (1 cc equals 0.1 mg of nitrogen as nitrite), avoiding material excess of sodium chlorid as a precipitant. Place a measured amount of 50 cc of one-hundredth normal potassium permanganate in a 5-inch porcelain evaporating dish, together with 200 cc of pure water and 25 cc of dilute sulphuric acid (1:4); warm to

50° C. and titrate with the standard solution of sodium nitrite, adding slowly, as the reduction of the permanganate is not instantaneous. One cubic centimeter of hundredth-normal permanganate is equivalent to 0.00077 gram of silver nitrite, hence 50 cc of the permanganate should be decolorized by exactly 35 cc of standard nitrite solution. (See Krauch, Chemical Reagents, Their Purity and Tests, p. 188.)

(2) Determination.

(a) *Method I.*—Select a series of 100 cc volumetric flasks of uniform dimensions and color. Place 2 grams of high-grade nitrite-free flour in each; add approximately 70 cc of nitrite-free distilled water and shake until the flour is thoroughly moistened.

From a burette containing the standard nitrite solution (c), add to the flasks containing the flour and water amounts of solution increasing by definite increments to form a series of standards for comparison having a range covering the probable nitrite content of the unknown sample. One flask should be reserved for a blank test. Where the quantity of nitrite present is small, the nitrite solution in the flasks may be increased by 0.4 cc each. Where bleaching is excessive, 1 gram of flour may be used throughout, or the standards may be given a wider variation in nitrite content.

In order to avoid making a large series of standards it is well to make a preliminary test to ascertain the approximate nitrite content of the unknown.

To each of two similar flasks add 2 grams of the flour to be tested and 90 cc of water; shake thoroughly and digest all of the flasks, including the blank, in a water bath at 40° C. for at least 15 minutes; add 2 cc of each of the Griess reagents, “(a)” and “(b),” to each flask. Continue the digestion at 40° C. for at least 20 minutes. The color should be developed in all flasks under conditions as nearly uniform as possible.

Make up to the marks with nitrite-free water and compare the unknown with the series of standards. This may best be done in a large, white, enameled pan, the effect of the turbidity, due to the flour, being minimized by the white background. The solutions should be allowed to subside and should not be shaken during comparison.

(b) *Method II.*—Weigh 20 grams of the flour into a 500 cc Erlenmeyer flask, add 200 cc of water, free from nitrites, previously warmed to 40° C., and close the flask with a rubber stopper. Shake vigorously for five minutes and digest for one hour in a water bath, keeping the temperature of the liquid in the flask at 40° C., and shaking at 10-minute intervals. Finally filter on a dry-folded filter free from nitrites. As the first portion of the filtrate is turbid, it should be returned to the filter and the operation repeated until a clear liquid is secured. Pipette 50 cc of the filtrate and, at the same time, 50 cc of the standard nitrite solution (c) into small flasks; add to each 50 cc of water 2 cc of solution (a) and 2 cc of solution (b), shake, and allow to stand one hour to bring out the color. Compare the two solutions in a colorimeter. Divide the height of the column of the standard solution by that of the solution of the sample, thus obtaining the parts of nitrogen as nitrous acid (free and combined) per million of flour.

A blank test should be made to establish the absence of nitrites in the water and filter paper, and care taken throughout the process to avoid contamination from nitrous fumes, gas flames, etc.

Practically the same results will be obtained if the digestion is made at 20° C. or at room temperature, but the method of solution as described above permits the determination of acidity by Mitchell's method in an aliquot of the same solution, provided the water used has previously been boiled in a Jena flask or narrow-mouthed tin vessel for five minutes or until neutral.

THE EFFECTS OF TIME AND TEMPERATURE OF DIGESTION ON THE AMOUNTS OF ACIDITY AND NITROUS NITROGEN EXTRACTED FROM FLOUR.

By A. L. WINTON and A. W. HANSEN.

Mitchell has shown that the results on the acidity of flour increase with the temperature of digestion up to 40° C. The following experiments were made to determine the effects of time, as well as temperature, on acidity determina-

tions, and also to learn the influence of these factors on the amounts of nitrites extracted. The purpose of the work was to learn whether both acidity and nitrous nitrogen can be determined in aliquots of the same solution.

METHODS.

METHODS OF SOLUTION.

Method 1.—Digest at 20° C. for one hour, shaking at the start. To 20 grams of flour contained in a 500 cc Erlenmeyer flask, add 200 cc of distilled water at 20° C., free from nitrites and previously boiled in a Jena flask until free from acidity. Stopper tightly, shake for five minutes, and allow to stand for one hour at 20° C. Decant the liquid on to a folded 24 cm S & S No. 588 filter paper, taking care not to disturb the flour at the bottom of the flask. Pass the first portion of the turbid filtrate through the paper a second time and repeat this operation until a clear filtrate is secured.

Method 2.—Digest at 20° C. for one hour, shaking at intervals. Proceed as in method 1, shaking the flask vigorously at 10-minute intervals in addition to the five minutes' shaking at the start.

Method 3.—Digest at 20° C. for two hours, shaking at intervals. Proceed as in method 2, except that the digestion is continued for two hours, shaking at 10-minute intervals.

Method 4.—Digest at 40° C. for one hour, shaking at intervals. Proceed as in method 2, except that water at 40° C. is employed and the digestion is carried on in a water bath at 40° C.

Method 5.—Digest at 40° C. for two hours, shaking at intervals. Proceed as in method 4, except that the digestion is continued for two hours, shaking at 10-minute intervals.

Method 1 is the same as described in Leach, Food Inspection and Analysis, second edition, page 322, except that the definite temperature, 20° C., is employed instead of room temperature. It is also essentially the same as described by Jago, in The Technology of Bread Making, page 768, except that the time of standing is one hour instead of one-half hour.

Method 4 is the same as that suggested by Mitchell, except that the directions as to shaking are more specific, and the digestion is conducted throughout at 40° C. instead of 10 minutes at 40° C. and the remainder of the time at room temperature.

DETERMINATION OF ACIDITY.

Titrate 50 cc of the clear filtrate, prepared as described in the foregoing sections, with tenth-normal phenolphthalein solution, using phenolphthalein as an indicator.

DETERMINATION OF NITROGEN AS NITROUS ACID.

Remove another portion of 50 cc of the clear filtrate and proceed as described on page 114, Method II.

RESULTS OF ANALYSES.

The determinations of acidity and nitrous nitrogen were made by the foregoing methods on four samples of bleached flour, two of hard wheat, heavy and light bleached, and two of soft wheat, heavy and light bleached. The results are given in the accompanying table.

It appears that for the determination of acidity 40° C. is the most satisfactory temperature of extraction, not only because the results are higher, but because this is the only temperature that is practicable in all laboratories and in all seasons. Digestion for one hour gave practically the same percentages of acidity as digestion for two hours, provided the flask was shaken at 10-minute intervals during the digestion.

The amount of nitrous nitrogen extracted was the same for digestion at 40° C. as for 20° C., and for one hour as for two hours; furthermore, shaking at the start extracted as much as shaking at intervals.

From the results obtained, method 4 appears to be the most practicable for the determination of acidity, and aliquots of this solution may be used for the determination of nitrous nitrogen.

Effects of time and temperature of digestion on the amounts of acidity and nitrous nitrogen extracted from flour.

Method.	Hard wheat, patent.				Hard wheat, clear.			
	Light bleached.		Heavy bleached.		Light bleached.		Heavy bleached.	
	Acidity as lactic acid.	Nitro- gen as nitrous acid.	Acidity as lactic acid.	Nitro- gen as nitrous acid.	Acidity as lactic acid.	Nitro- gen as nitrous acid.	Acidity as lactic acid.	Nitro- gen as nitrous acid.
Digested at 20° C:	<i>Per cent.</i>	<i>Parts per million.</i>	<i>Per cent.</i>	<i>Parts per million.</i>	<i>Per cent.</i>	<i>Parts per million.</i>	<i>Per cent.</i>	<i>Parts per million.</i>
1-hour digestion—								
Shaken at start.....	0.072	0.40	0.077	3.04	0.165	0.32	0.198	2.92
Shaken at intervals.....	.113	.42	.113	3.00	.243	.30	.263	3.00
2-hour digestion, shaken at in- tervals.....	.108	.42	.113	3.04	.243	.30	.267	2.96
Digested at 40° C:								
1-hour digestion, shaken at in- vals.....	.126	.40	.126	3.04	.293	.32	.293	2.92
2-hour digestion, shaken at in- tervals.....	.126	.42	.131	3.04	.306	.32	.303	2.92

Method.	Soft wheat, patent.				Soft wheat, clear.			
	Light bleached.		Heavy bleached.		Light bleached.		Heavy bleached.	
	Acidity as lactic acid.	Nitro- gen as nitrous acid.	Acidity as lactic acid.	Nitro- gen as nitrous acid.	Acidity as lactic acid.	Nitro- gen as nitrous acid.	Acidity as lactic acid.	Nitro- gen as nitrous acid.
Digested at 20° C:	<i>Per cent.</i>	<i>Parts per million.</i>	<i>Per cent.</i>	<i>Parts per million.</i>	<i>Per cent.</i>	<i>Parts per million.</i>	<i>Per cent.</i>	<i>Parts per million.</i>
1-hour digestion—								
Shaken at start.....	0.090	0.40	0.090	2.72	0.162	0.32	0.153	2.23
Shaken at intervals.....	.117	.38	.117	2.72	.189	.34	.202	2.23
2-hour digestion, shaken at in- tervals.....	.122	.38	.122	2.68	.196	.32	.212	2.23
Digested at 40° C:								
1-hour digestion, shaken at in- tervals.....	.131	.40	.131	2.72	.207	.34	.225	2.32
2-hour digestion, shaken at in- tervals.....	.131	.38	.136	2.72	.216	.34	.230	2.32

A RECALCULATION OF JUCKENACK'S EGG-NOODLE TABLES.

By R. W. HILTS.

The work of Juckenack¹ on the analysis of egg noodles and the estimation of their egg content by the determination of lecithin phosphoric acid has received quite general recognition. His tables for estimating the number of eggs to the pound of flour can not, however, be used without restriction for the English weight system. Although the author does not so state, an examination of the formulas by which the tables were calculated shows that the

¹ Zts. Nahr. Genussm., 1900, 3: 1, 11.

basis is a so-called "pound" of 500 grams. Though the difference is insignificant in the lower figures of the tables, it would lead to some error with noodles containing much egg. For convenience Juckennack's tables have accordingly been recalculated on the basis of the avoirdupois pound of 453.59 grams, using otherwise the same formulas and fundamental values.

Recalculated tables.

For use with whole eggs.					For use with yolks.				
Number of eggs to 1 pound of flour.	Average data on dry matter of such noodles.				Number of yolks to 1 pound of flour.	Average data on dry matter of such noodles.			
	Ash.	Phosphoric acid.		Protein (N×6.25).		Ash.	Phosphoric acid.		Protein (N×6.25).
		Total.	Lecithin.				Total.	Lecithin.	
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>		<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
0	0.460	0.230	0.0225	12.00	0	0.460	0.230	0.0225	12.00
$\frac{1}{2}$.518	.253	.0385	12.55	$\frac{1}{2}$.475	.253	.0388	12.20
1	.575	.275	.0541	13.08	1	.491	.276	.0548	12.41
2	.684	.318	.0840	14.11	2	.521	.321	.0858	12.80
3	.786	.359	.1120	15.07	3	.550	.364	.1157	13.18
4	.883	.397	.1385	15.97	4	.578	.405	.1445	13.54
5	.974	.433	.1636	16.83	5	.604	.445	.1722	13.89
6	1.061	.468	.1874	17.65	6	.630	.453	.1990	14.22
7	1.143	.500	.2099	18.42	7	.655	.520	.2248	14.55
8	1.221	.531	.2314	19.15	8	.680	.556	.2497	14.87
9	1.295	.560	.2517	19.85	9	.703	.591	.2738	15.17
10	1.366	.588	.2711	20.52	10	.725	.624	.2971	15.47

It was necessary to find by calculation from the original tables the basic values assumed for ash and protein in the egg yolk and whole egg. These were found to be based on the averages of König,¹ as are all the other values for the egg with the exception of total and lecithin phosphoric acid, which Juckennack took from his own work. The flour is assumed to contain an average of 13.05 per cent of moisture, with dry matter of the composition shown at the top of the tables.

NOTE ON DETERMINATION OF TIN IN FOODS.

By A. W. HANSEN and L. C. JOHNSON.

The writers do not wish to claim credit for any new principles in the method here outlined; all available information was utilized. The use of nitric and sulphuric acid to carbonize the organic matter is essentially the procedure followed in the Marsh-Berzelius-Sanger arsenic method, and in the Smith-Bartlett² tin method, except that dilute acids are used, which greatly reduces the danger of loss from frothing. A description of the method follows:

Method of making solution.—Place in a Kjeldahl flask an amount of the sample containing about 25 grams of solid matter. Add some pieces of broken glass, about 200 cc of water, 100 cc of concentrated nitric acid, and 50 cc of concentrated sulphuric acid. Heat cautiously over a wire gauze. Continue alternately adding nitric acid and heating till all organic matter is destroyed, as evidenced by the absence of charring, and boil down the solution to a small volume. Finally add about 25 grams of potassium sulphate and heat till all

¹ *Chemie der Menschlichen Nahrungs und Genusmittel*, 4th ed., vol. 1, pp. 98–99; vol. 2, p. 573.

² U. S. Dept. Agr., Bureau of Chemistry Bul. 137, p. 136.

nitric acid is driven off, adding more sulphuric acid if necessary. This method of making the solution could doubtless be used to advantage in determining copper, lead, and zinc in foods.

Determination of tin.—Transfer the sulphuric acid solution to a liter Erlenmeyer flask, dilute to about 600 cc, and pass in hydrogen sulphid. Let stand overnight. Filter off sulphids and wash with hot water. Digest filter and precipitate with hot sodium sulphid, filter, and wash with hot water.

Barely acidify filtrate from the sodium sulphid treatment with hydrochloric acid. Filter off the tin sulphid, wash with hot water, ignite, and weigh as tin oxid. (Factor for metallic tin, 0.78808.)

REPORT ON CONDIMENTS OTHER THAN SPICES.

By W. J. McGEE, *Associate Referee.*

After some correspondence and discussion it was decided to devote the work done under the head of condiments other than spices to ketchup. An outline for the chemical examination of ketchup had been sent to each of the branch laboratories in circular letter from the Bureau of Chemistry, dated February 18, 1911. These methods were as follows:

STATEMENT OF METHODS.

Total solids.—Determine as usual, using from 3 to 5 grams and drying at the temperature of boiling water for 4 hours. The sample should be spread out in a thin layer for drying.

Insoluble solids.—Wash 20 grams repeatedly with hot water, centrifuging after each addition of water. Pour the clear supernatant liquid through a tared double filter on a Büchner funnel. A cylinder 1 to 1½ inches in diameter and 5 to 6 inches long is convenient for washing and centrifuging. This may be prepared by shortening a colorimeter tube. After four or five washings transfer the remaining insoluble matter to the filter and finally dry for two hours at 100° C. The filter paper used in this determination should be dried for two hours at 100° before the original weighing.

Soluble solids.—Calculated by difference.

Ash.—Determine in the usual manner. Avoid heating above dull redness.

Alkalinity of ash.—Transfer the ash to a 100 cc flask and dilute to the mark. This solution, together with a small amount of insoluble matter, is shaken thoroughly and an aliquot portion pipetted off as quickly as possible for the determination of alkalinity of the ash. Determine as under "Alkalinity of Insoluble Ash," Bulletin No. 107, Revised, page 69, and report as cubic centimeters of tenth-normal acid per ash of 1 gram of ketchup. Also report as per cent potassium carbonate in the salt-free ash.

Sodium chlorid.—Determine on an aliquot portion of the ash solution by Mohr's method.

Reducing sugars before inversion.—Weigh 10 grams into a 100 cc flask, clarify with an excess of normal lead acetate, dilute to the mark, and filter. Remove the excess of lead with dry sodium sulphate or sodium carbonate, filter, and determine reducing sugars by the Munson and Walker method, Bulletin 107, Revised, page 242. Calculate the sugars as per cent invert sugar and sucrose. (See table in Bul. 107, Rev., pp. 243-251, column 5.)

Reducing sugars after inversion.—Transfer 50 cc of the filtrate obtained in the previous determination to a 100-cc flask, add 5 cc concentrated hydrochloric acid, let stand overnight, neutralize exactly with sodium hydroxid, cool, make to the mark and determine reducing sugars as before. Calculate as invert sugar.

Sucrose.—Calculate as directed on pages 41 and 42 of Bulletin 107, Revised.

Polarization after inversion.—Determine in the usual manner. Use the normal weight of ketchup and allow to stand overnight at room temperature for inversion. Report as polarization on the normal weight, that is, 26 grams in 100 cc.

Total acids as citric.—Use 5 grams and determine as under "Vinegar," Bulletin 107, Revised, page 103. (1 cc of tenth-normal alkali = 0.0063 gram of citric acid.)

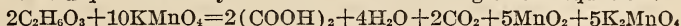
Volatile acids as acetic.—Determine volatile acids in the usual manner, using 25 grams of sample. (1 cc of tenth-normal alkali=0.006 gram of acetic acid.) Reserve the neutralized distillate for the determination of butyric and formic acids.

Butyric acid.—Evaporate to dryness the neutralized distillate obtained under "Volatile acids," in a weighed platinum dish on the steam bath. Heat for 2 hours in an oven at 100° C. and weigh. From the alkali used and the weight of the salts calculate the per cent of sodium in the salts. Decompose the salts with about 5 cc of 10 per cent sulphuric acid. The acid residue thus obtained should be smelled to ascertain the presence of butyric acid. The sodium content of sodium acetate is 28 per cent, while that of sodium butyrate is 20.5. Owing to the natural limits of error, a lower sodium content than 28 per cent may occur even in the absence of butyric acid, but if the amount of sodium present in the salt is found by the calculation directed above to be as low as 27 per cent, it is our experience that a considerable amount of butyric acid is present. A much smaller amount can be detected by smell, however, and this method of calculation is only of value in determining the approximate amount of butyric acid where considerable quantities are present.

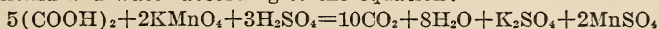
Formic acid.—Test for formic acid as follows: To the salt residue acidified with sulphuric acid obtained in the preceding determination small quantities of magnesium are added, the action of the magnesium upon the acid being allowed to continue for about an hour. Formic acid present is thus reduced to formaldehyde, which may be detected by the Hehner or Leach method. If the reaction is positive the presence or absence of formaldehyde in the original sample should be demonstrated.

Fixed acids as citric.—Calculate by difference.

Lactic acid.—Make 100 grams up to 500 cc with water, mix thoroughly, centrifuge, and take 400 cc of the clear portion. Evaporate this to about 100 cc, add 10 cc of 20 per cent normal lead acetate solution, filter, and wash the precipitate twice with a small amount of water. To the filtrate add a moderate excess of sulphuric acid, filter, wash the precipitate with a small amount of water, and evaporate the filtrate on the steam bath to a convenient volume for extraction in a continuous liquid extractor. In this laboratory this volume is 100 cc. Extract for 18 to 20 hours in a liquid extractor with washed ether. (Ether sufficiently pure for this purpose may be prepared by shaking out ordinary ether once with a sodium hydroxid solution and then 10 times with small quantities of water.) To the ether extract is added about 20 cc of water, and the ether is evaporated. Care must be taken to remove all traces of ether. The water is added before evaporation because of the possible presence of traces of sulphuric acid which might otherwise char the lactic acid. Approximately 3 grams sodium hydroxid are then added to the water solution and 50 cc of a 1.5 per cent solution of potassium permanganate are added from a pipette. This is heated on a water bath at 100° for one-half hour. At the end of that time, or before, if the color is not a decided blue black or purple, but is green or colorless above the layer of brown precipitate, more standard permanganate in measured portions is added until, after heating one-half hour on a boiling-water bath, the color is a blue black or purple. The oxidation is then complete. The hot solution is strongly acidified with dilute sulphuric acid and about 50 cc of 10 per cent sulphuric acid, and standard oxalic acid is run in from a burette until the solution is decolorized. In this laboratory a 5 per cent solution of oxalic acid is used for that purpose. Any slight excess of oxalic acid is titrated back with the same standard permanganate solution. It should be understood that any standard permanganate and oxalic acid solutions may be used within reasonable limits of strength. In alkaline solution the permanganate oxidizes the lactic acid quantitatively to oxalic acid according to the equation:



In acid solution the oxalic acid is further oxidized by the permanganate to carbon dioxide and water according to the equation:



Calculation: The total weight of permanganate used in the oxidation of the lactic acid is determined by subtracting the permanganate equivalent of the oxalic acid used from the total amount used. The weight of permanganate times 0.237 equals the weight of lactic acid.

Citric acid.—Weigh 25 grams into a 250-cc beaker, make up to approximately 200 cc with 95 per cent alcohol, allow to stand with frequent stirring for four hours, filter through a folded filter and wash with 50 cc of 80 per cent alcohol.

To the filtrate add 10 cc of 20 per cent barium acetate solution, stir well with a glass rod, allow to stand overnight. In the morning filter on a Gooch crucible, washing with 50 per cent alcohol, dry 2 hours in an oven at 100° C. and weigh. Weight of precipitate $\times 0.49$ equals citric acid.

Nitrogen.—Determine as usual.

Protein.—Calculated. (Nitrogen $\times 6.25$.)

Ammonia by distillation with magnesium oxid.—Make 50 grams up to 300 cc with distilled water, add 10 grams magnesium oxid, place in a 1-liter distilling flask, and distil 100 cc in approximately 30 minutes, running the distillate into standard acid. Titrate the excess of acid with tenth-normal sodium hydroxid, using cochineal or methyl orange as an indicator. (1 cc of tenth-normal hydrochloric acid = 0.0017 gram NH_3 .)

Nitrogen partition with basic lead acetate.—Weigh into a 250 cc beaker 25 grams of the sample. Make up to 200 cc with water, add 10 cc 20 per cent basic lead acetate, mix thoroughly, filter through a folded filter, and determine nitrogen by the Kjeldahl method in an aliquot portion of the filtrate. For this purpose it is well to use as large an amount of filtrate as possible. Calculate this nitrogen as per cent total nitrogen in the original ketchup. From the total nitrogen of the ketchup calculate the quantity of nitrogen in the basic lead acetate precipitate.

Pectin determination.—Filter the ketchup through a folded filter and weigh 25 grams of the filtrate into a 250 cc beaker. Add 95 per cent alcohol to a total volume of 200 cc. Mix thoroughly, allow to stand overnight. The so-called pectin bodies will probably be found firmly sticking to the sides and bottom of the beaker. If this is the case, pour off the alcohol, dissolve the pectins in a small amount of warm water, transfer to a large platinum dish, make up to approximately 100 cc with 95 per cent alcohol, and allow to stand 12 hours. Pour off the alcohol, dry the pectins contained in the dish for 2 hours in an oven at 100°, and weigh. Ash at a dull red heat, weigh and subtract the weight of the ash. The loss on ignition represents the so-called pectin bodies for a 25-gram sample.

Sand.—Weigh 100 grams into a 2 or 3 liter beaker, nearly fill the beaker with water and mix the contents thoroughly. Allow to stand five minutes and decant the supernatant liquid into a second beaker; refill the first with water and again mix the contents. After five minutes more, decant the second beaker into the third, the first into the second, refill, and again mix the first. Continue this operation, decanting from the third beaker into the sink, until the lighter material is washed out from the ketchup; then collect the sand from the three beakers in a tared Gooch crucible. Dry, ignite, and weigh. Your attention is especially called to the fact that under "sand" should only be reported the figure obtained by this method. The results obtained by the determination of ash insoluble in hydrochloric acid are not applicable to the determination of sand in tomato ketchup, partly because the percentage present is so small and the sand is so unevenly distributed that reliable results can only be obtained by taking a larger sample than is possible in the determination of ash.

Qualitative determinations.—Make qualitative examinations for benzoic acid, saccharin, boric acid, starch.

Report also the following.—Sugar-free, salt-free soluble solids; ratio of insoluble solids to sugar-free, salt-free soluble solids; ratio of nitrogen in lead acetate filtrate to total nitrogen; ratio of ammoniacal nitrogen to total nitrogen; ratio lactic acid to citric acid; ratio citric acid to sugar-free, salt-free soluble solids; ratio total protein to sugar-free, salt-free soluble solids.

Examine the original sample before mixing and report the presence and appearance of any sediment which may appear on the bottom.

ANALYTICAL RESULTS.

For purposes of investigation two samples of ketchup were prepared after a cookbook recipe; one was made from clean, sound, ripe tomatoes with stems and spots cut out, and the other was made from tomatoes which had been kept in the laboratory spread out on the bench until every one had started to decay—some were covered with a green mold. Owing to the very large amount of spices demanded by this recipe the two samples of ketchup tasted practically alike.

The sample made from sound tomatoes was designated "A," that from decayed tomatoes "B." Three pints of each of these were sent to four col-

laborators, who were requested to make a complete analysis according to the methods just given.

Reports were received from two of the collaborators and these, with the referee's own results, have been tabulated as follows:

Comparative percentage results by three analysts on two samples of ketchup.

Determinations.	"A" samples (sound tomatoes).			"B" samples (decayed tomatoes).		
	1	2	3	1	2	3
Total solids.....	23.80	23.69	22.90	18.93	19.21	19.67
Insoluble solids.....	2.39	2.38	2.25	1.83	1.80	1.88
Soluble solids.....	21.41	21.31	20.65	17.10	17.41	17.79
Ash.....	2.74	2.80	2.77	2.46	2.42	2.37
Alkalinity of ash (per cent potassium carbonate in salt-free ash).....	56.8	60.3	43.6	54.6	72.0	25.7
Alkalinity of ash (cc tenth-normal acid in original ketchup).....	.848	.900	.700	.871	1.0	.40
Sodium chloride.....	1.71	1.77	1.66	1.34	1.46	1.24
Reducing sugars before inversion.....	13.10	13.92	13.76	8.00	8.39	8.78
Reducing sugars after inversion.....	14.70	15.56	15.36	11.95	12.52	12.67
Polarization after inversion ($^{\circ}$ V.).....	31 $^{\circ}$ C. (-5.5	30.5 $^{\circ}$ C. -6.2	33.5 $^{\circ}$ C. -5.0	33.5 $^{\circ}$ C. -4.2	30 $^{\circ}$ C. -4.6	30 $^{\circ}$ C. -4.0
Sucrose.....	1.50	1.56	1.52	3.75	3.92	3.50
Total acids, as citric.....	2.56	2.37	2.21	2.29	2.19	2.23
Fixed acids, as citric.....	1.05	1.17	.62	.63	.79	.68
Volatile acids, as acetic.....	1.43	1.15	1.40	1.58	1.33	1.45
Butyric acid.....	Present.	None.	Present.	None.
Formic acid.....	None.	Present.	None.	Present.
Lactic acid.....	.20	.39	.28	.559	.63	.32
Citric acid.....	.502	.480	.570	.354	.40	.510
Nitrogen.....	.338349	.269223
Protein (N \times 6.25).....	2.11	2.18	1.68	1.39
Ammonia by distillation with magnesium oxid.....	.0612	.0580	.056	.0228	.019	.019
Nitrogen partition with basic lead acetate.....	.263268	.103137
Pectin determination.....	1.17	1.37	.97	.75	.91	.94
Sand.....	.0133026	.017008
Saccharin, qualitative.....	None.	None.	None.	None.
Boric acid, qualitative.....	None.	None.	None.	None.
Benzoic acid, qualitative.....	None.	None.	None.	None.
Starch, qualitative.....	None.	None.	None.	None.
Sugar-free, salt-free soluble solids.....	5.10	4.06	3.71	4.01	3.64	4.27
Ratio of insoluble solids to sugar-free, salt-free soluble solids.....	1:2.13	1:1.70	1:1.65	1:2.19	1:2.02	1:2.26
Ratio of nitrogen in basic lead acetate filtrate to total nitrogen.....	1:1.28	1:1.30	1:2.61	1:1.62
Ratio of ammoniacal nitrogen to total nitrogen.....	1:6.71	1:7.59	1:14.34	1:14.
Ratio lactic acid to citric acid.....	1:2.51	1:1.29	1:2.02	1:0.63	1:0.63	1:1.6
Ratio citric acid to sugar-free, salt-free soluble solids.....	1:10.10	1:8.46	1:6.51	1:11.32	1:9.10	1:8.37
Ratio of total protein to sugar-free, salt-free soluble solids.....	1:2.41	1:1.70	1:2.40	1:3.07
Sediment before opening.....	None.	None.	None.	None.

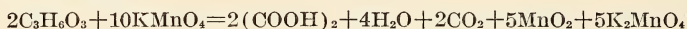
DISCUSSION OF RESULTS.

The agreement between the different analysts is fair, except in the determinations of alkalinity of ash, per cent of potassium carbonate in the salt-free ash, and of citric and lactic acids. The number of collaborators was not large enough to allow any definite conclusions to be drawn. The results, however, show the desirability of further work on the determination of lactic and citric acids. The work done in the Bureau of Chemistry by Bacon and Dunbar has demonstrated the value of the lactic-citric ratio in interpreting a ketchup analysis. It is of considerable importance that a method be worked out that will give reasonably consistent results in the hands of operators of ordinary skill.

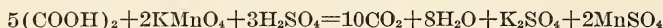
I would suggest that the lactic-acid method be modified up to the point of the ether extraction in the following manner:

Make 100 grams of ketchup up to 500 cc with water, mix thoroughly, centrifuge; pour off 400 cc through a filter, add 10 cc of 20 per cent lead acetate

solution, and make up to 500 cc. After centrifuging again 400 cc should be poured off through a filter and a slight excess of dilute sulphuric acid added. Settle precipitate with centrifugal and pour directly into evaporating dish. Wash the lead sulphate, precipitate once with about 50 cc of water, and filter into the evaporating dish. Evaporate on steam bath to volume desired for the extraction apparatus. Extract for 18 to 20 hours in a liquid extractor with washed ether. (Ether sufficiently pure for this purpose may be prepared by shaking out ordinary ether once with a sodium hydroxid solution and then 10 times with small quantities of water.) To the ether extract is added about 20 cc of water and the ether is evaporated. Care must be taken to remove all traces of ether. The water is added before evaporation because of the possible presence of traces of sulphuric acid which might otherwise char the lactic acid. Approximately 3 grams sodium hydroxid are then added to the water solution and 50 cc of a 1.5 per cent solution of potassium permanganate are added from a pipette. This mixture is heated on a water bath at 100° C. for one-half hour. At the end of that time, or before, if the color is not a decided blue-black or purple, but is green or colorless above the layer of brown precipitate, more standard permanganate in measured portions is added, until, after heating one-half hour on a boiling water bath, the color is a blue-black or purple. The oxidation is then complete. The hot solution is strongly acidified with dilute sulphuric acid, about 50 cc of 10 per cent sulphuric acid, and standard oxalic acid run in from a burette until the solution is decolorized. In this laboratory a 5 per cent solution of oxalic acid is used for that purpose. Any slight excess of oxalic acid is titrated back with the same standard permanganate solution. It should be understood that any standard permanganate and oxalic acid solutions may be used within reasonable limits of strength. In alkaline solution, the permanganate oxidizes the lactic acid quantitatively to oxalic acid according to the equation:



Then in acid solution, the oxalic acid is further oxidized by the permanganate to carbon dioxid and water according to the equation:



Calculation: The total weight of permanganate used in the oxidation of the lactic acid is determined by subtracting the permanganate equivalent of the oxalic acid used from the total amount used. The weight of permanganate times 0.237 equals the weight of lactic acid.

Better results are obtained if the ether extract is run down to dryness, taken up with water, and filtered before adding the alkali and permanganate.

RECOMMENDATION.

It is recommended—

(1) That these methods or modifications of them be tried another year, if possible, securing a much larger number of collaborators.

(2) That some experiments be tried to ascertain to what extent the nitrogen ratios can be influenced by the spice content of ketchup.

(3) That, as the complete scheme of analysis as outlined is very long and takes about 16 hours of practically continuous attention, a special attempt be made to eliminate all the determinations not actually necessary for the judging of a ketchup.

REPORT ON COLORS.

By W. E. MATHEWSON, *Associate Referee*.

In the cooperative work on colors done last year two problems were considered—the identification of the permitted coal-tar colors when used in admixture with each other and the identification of certain other dyes that for one reason or another seemed to merit special study. This season an examination has been made of methods used for separating and identifying nonpermitted colors in admixtures.

Samples of six artificially colored food products were sent out, together with the statement of a procedure used in the New York laboratory for dealing with

such mixtures. This consists in making the samples strongly acid with hydrochloric acid (about one-third the volume of concentrated acid being added) and shaking out with a few portions of amyl alcohol. The alcohol extracts are combined, then shaken with a number of small portions of hot water. The amyl alcohol is then diluted with gasoline, given a few more washings with water, and finally treated with very dilute caustic soda. In general the higher sulphonated dyes are found in the first strongly acid washings, those of a lower degree of sulphonation appearing later. If the original mixture contained basic colors, these are first removed by making alkaline and shaking with ether, the ether solution of the color bases being then fractionated in a similar way by washing with water and finally with dilute acid.

The colors used in preparing samples are given in the following table:

Samples for the identification of nonpermitted colors in admixtures.

Number.	Food product.	Coloring matters.	S. and J. numbers.
1.....	Imitation cordial.....	Bordeaux B.....	65
		Erythrosin.....	517
2.....	do.....	Tartrazin.....	94
		Crocein Orange.....	13
3.....	do.....	Light Green SF Yellowish.....	435
		Acid Yellow G.....	8
4.....	do.....	Rhodamin B.....	504
		Methyl Violet.....	451
5 ¹	do.....	Indigo Carmin.....	692
		Amaranth.....	107
		Naphthol Yellow S.....	4
6.....	Salad oil.....	Sudan II.....	49
		Anilin Yellow.....	7

¹ Examination of Sample No. 5 some six weeks after its preparation showed that the indigo carmin had entirely disappeared.

All these dyes are known to be frequently used in foods, and all, with one or two possible exceptions, have been found in admixture with other colors. Since most methods of separation are more or less troublesome with impure dyes, commercial products were used in preparing the samples, excepting the Crocein orange, acid yellow, and the oil-soluble colors, which were made in the laboratory. The acid yellow, however, was prepared in the usual way by sulphonating aminoazobenzene, and hence corresponded to No. 8 of the Schultz-Julius-Green tables, a mixture of sulphonated derivatives. The results obtained are given below:

Cooperative results on color mixtures.

Analyst.	Coloring matters reported.		
	Sample 1.	Sample 2.	Sample 3.
E. H. Grant, New Orleans, La.	Erythrosin.....	Crocein Orange.....	Light Green SF Yellowish.
	Amaranth.....	Tartrazin.....	Metanil Yellow.
C. S. Brinton, Philadelphia, Pa.	Bordeaux B.....	Crocein Orange.....	Light Green SF Yellowish.
	Erythrosin.....	Tartrazin.....	Acid Yellow G.
H. M. Loomis, Seattle, Wash.	Bordeaux B.....	Crocein Orange.....	Light Green SF Yellowish.
	Erythrosin.....	Tartrazin.....	Acid Yellow G.
W. A. Brannon, Washington, D. C.	Bordeaux B.....	Crocein Orange.....	Light Green SF Yellowish.
	Erythrosin.....	Tartrazin.....	Acid Yellow G.
	Bordeaux B.....	Crocein Orange.....	Light Green SF Yellowish.
A. M. Doyle, Washington, D. C.	Erythrosin.....	Tartrazin.....	Acid Yellow G.
	Rhodamin B (trace).....

Cooperative results on color mixtures—Continued.

Analyst.	Sample 4.	Sample 5.	Sample 6.
E. H. Grant, New Orleans, La.	{Methylene Blue..... Rhodamin B.....	Naphthol Yellow S..... Amaranth.....	Sudan I. Butter Yellow (trace).
C. S. Brinton, Philadelphia, Pa.	{Methyl Violet..... Rhodamin B.....	{Naphthol Yellow S..... Amaranth..... Indigo Carmin.....	Sudan I. Anilin Yellow.
H. M. Loomis, Seattle, Wash.	{Crystal Violet..... Rhodamin B.....	{Naphthol Yellow S..... Indigo Carmin.....	Sudan I. Anilin Yellow.
W. A. Brannon, Washington, D. C.	{Methyl Violet..... Rhodamin B.....	Naphthol Yellow S..... Amaranth.....	Benzeneazo-a-naphthyl-amin.
G. M. Bartlett, Boston, Mass.	Similar to Anilin Yellow.
A. M. Doyle, Washington, D. C.	{Methyl Violet..... Rhodamin B.....	Naphthol Yellow S..... Amaranth.....	Sudan I. Unidentified Yellow.

Details as to the methods of separation and identification used were not stated in most cases, but apparently immiscible solvents were usually employed for the separation and the dyes subsequently identified by their spot reactions when dyed on wool, etc., applying data given in United States Department of Agriculture Circular No. 63, Allen, and other sources.

C. S. Brinton used glacial acetic acid (Cornellison's method) for extracting the coloring matter from the oil in Sample No. 6. E. H. Grant also followed this procedure, but prefers to saponify the oil directly. W. A. Brannon saponified the oil, but found it difficult to obtain a clean ether solution of the coloring matter. G. M. Bartlett dissolved the oil in ether and shook out with strong hydrochloric acid.

H. M. Loomis suggests that the amyl alcohol or ether solution of the colors obtained on shaking out the original mixture should be washed with acid or alkali (as the case may be) to remove sugar, etc., before beginning the fractional shaking out with water.

As the permitted colors are so much more frequently used than others, any satisfactory general method for the treatment of unknown mixtures must require no great amount of manipulation or time when only these are present. Usually, however, the main object of the work is to determine whether or not nonpermitted dyes have been used, the identification of others being of interest only as bearing on this question. Such a method, therefore, should involve a minimum use of reagents likely to destroy or alter chemically any of the coloring matters and should be of such character that the deportment of the dye may be predicted with some accuracy from its constitution. Also it must be capable of being adapted to mixtures containing relatively small amounts of one component. These requirements seem best satisfied, on the whole, by the use of immiscible solvents.

Dichlorhydrin, suggested as a solvent by H. A. Seil, has been given some comparative study.¹ Of most dyes it extracts from a solution of given acidity much less than does amyl alcohol. However, it takes up far more Light Green SF Yellowish (and similar acid greens) than the latter solvent, and is useful for separating these after the other colors have been removed.

T. M. Price's recent paper² describing a separation of the permitted colors in dry mixtures gives new analytical data, but probably did not appear early enough to be made use of in the cooperative work.

It is suggested that the study of the separation of mixtures be continued by the association and that work bearing on the identification of the common natural coloring matters be begun.

¹ U. S. Department of Agriculture, Bureau of Chemistry Cir. 89.

² U. S. Department of Agriculture, Bureau of Animal Industry Cir. 180.

REPORT ON VINEGAR.

By W. A. BENDER, *Associate Referee*.

No cooperative work was done this year on vinegar, the referee's work having consisted in a revision of the provisional methods, which is recommended for the reason that new methods of importance have been in use for some time, and modifications have been made in some of the older methods. The referee considers it highly important to bring the provisional methods up to date with the least possible delay and a revision is therefore submitted for adoption and further study.

The methods were first written up substantially the same as those sent out last year by R. E. Doolittle with samples to the various Government laboratories, and copies were sent to representative food chemists throughout the country with a request for criticism. With these criticisms in mind the final copy was prepared. The methods as herein presented, except section 9, have been used for a year and a half in the New York and Washington laboratories of the Bureau of Chemistry, and were tested last year in conjunction with the referee's work and are mentioned in his report. (See Bul. 137, pp. 59, 60, and 61.) In case they are adopted the most important changes that will be effected in the methods as now printed in Bulletin 107, Revised, are as follows:

1. *Addition of the glycerin determination.*—This determination as worked out and tested by Ross in the case of wine and vinegar has been incorporated without change. Its accuracy has been further tested by both E. H. Goodnow and the referee, separately and together. It has been further shown by extensive work done in vinegar factories by the referee and Mr. Goodnow under the supervision of Messrs. Tolman and Doolittle that it is an essential determination for judging the purity of a vinegar. In Judge Willard's decision, at the recent vinegar trial in Minneapolis, it was held that the evidence showed this method to be accurate and essential.

2. *Reducing sugars direct after evaporation.*—It is a well-known fact that vinegar contains varying amounts of volatile reducing bodies, which are incorrectly estimated as sugar in the method formerly used. To get the true amount of sugar present it is, therefore, necessary to drive off this volatile matter by evaporation and use the residue for the determination. Clarification and neutralization are omitted following the referee's suggestion of last year.

3. *Fixed acid* is determined by titration of the residue obtained after repeated evaporation. The objection to the present method of Bulletin 107, Revised, is the difficulty of an accurate estimation of volatile acid by steam distillation.

4. *Estimation of color by the brewer's scale.*

5. *Determination of color removed by fuller's earth* is added for the reason that it is of value in the case of the addition of a large amount of caramel to a diluted vinegar.

6. *The alcohol precipitate* has been shown to be of value in detecting products made from decomposed pomace, waste, or apples. The referee believes that further cooperative work should be done on this method.

7. *The pentosan determination* is made for the same reason as stated in the preceding paragraph. This is a standard method which gives concordant results, and is extremely valuable in cases where material unfit for consumption has been used.

The following determinations given in Bulletin 107, Revised, have been omitted from the present revision:

12. Oxalic acid; 13 and 14, detection of bitartrate of potassium and free tartaric acid; 15 and 16, detection and determination of free mineral acids; 19, detection of dextrin; 20, detection of coloring matters, and 22, detection of

foreign pungent materials. The referee does not know that any recent work has been done along these lines and personally does not feel able to include them in the recommendations, but sees no objection to leaving them as they stand until question arises as to their value.

RECOMMENDATIONS.

It is recommended—

(1) That method 5 for glycerin by S. H. Ross be adopted provisionally, as published in the Proceedings for 1910. (Bul. 137, pp. 61–63.)

(2) That method 21 for pentosans be adopted provisionally. (This is the provisional method of Bulletin 107, Revised, p. 54, applied to vinegar with the direction for the use of the proper amount of hydrochloric acid to account for the water of the vinegar.)

(3) That the other new methods and modifications submitted be printed and studied further during the coming year.

METHODS FOR THE ANALYSIS OF VINEGAR.

1. *Preparation of sample.*—For microscopical examination employ the original sample, but for chemical analysis filter if turbid.

2. *Calculation of results.*—Express all results as grams per 100 cc.

3. *Specific gravity.*—Determine as directed under XIII, wine, page 83, Bulletin 107, Revised.

4. *Alcohol.*—Measure 100 cc of the sample into a round-bottom distilling flask. Make faintly alkaline with saturated caustic soda solution, add a small scrap of paraffin, distil almost 50 cc, make up to 50 cc at temperature of sample, filter if necessary, and determine specific gravity by pycnometer or Sprengel tube. Calculate per cent by volume, or grams per 100 cc, from Table II, page 203, bearing in mind that the alcohol strength of the distillate is twice that of the original vinegar.

5. *Glycerin.*—Ross's method. Bulletin 137, page 61.

6. *Solids.*—Measure 10 cc of filtered vinegar into a tared flat-bottom platinum dish of 50 mm diameter, evaporate on the water bath to a thick sirup and dry for exactly two and one-half hours in the drying oven at the temperature of boiling water; cool and weigh. It is essential to use a flat-bottom dish.

7. *Total reducing matters before inversion.*—Proceed according to Munson and Walker's method (Bul. 107, Rev., p. 241), using 10 or 20 cc of sample. Express results as grams of invert sugar per 100 cc. Malt vinegar should be clarified with sodium phosphotungstate.

8. *Reducing sugars before inversion, after evaporation.*—Evaporate 50 cc to 5 cc on the water bath. Add 25 cc water and evaporate to 5 cc. Again add 25 cc water and evaporate to 5 cc. Transfer to a volumetric flask, make up to the mark, and proceed as under "7," using a quantity equivalent to 10 or 20 cc of sample.

9. *Reducing sugar after inversion.*—Proceed as under "8." After the last evaporation to 5 cc transfer to a 100 cc flask with 70 cc of water and invert by one of the methods given under "VI. General methods" (c), page 40. Nearly neutralize with caustic soda, make up to the mark and proceed as under "7," using a quantity equivalent to 10 or 20 cc of sample.

10. *Polarization.*—If the lead precipitate is heavy add to 50 cc of sample 5 cc of lead subacetate solution, shake and let stand 30 minutes, filter and polarize, preferably in a 200 mm tube, correcting for dilution. If lead subacetate gives only a turbidity, add to the 50 cc sample in flask 10 cc alumina cream, shake, let stand 30 minutes, filter, and polarize, correcting for dilution.

11. *Ash.*—Measure 25 cc into a tared platinum dish, evaporate to dryness on the steam bath, heat in the muffle at low heat to expel inflammable gases, treat the charred portion with a few cubic centimeters of water and evaporate dry on the bath; replace in the muffle at low redness for 15 minutes, and continue the alternate evaporation and heating until a white or gray ash is obtained, at no time allowing the temperature to exceed a dull red; cool in desiccator and weigh.

12. *Solubility and alkalinity of soluble ash.*—Add to the above ash about 10 to 15 cc distilled water, bring to a boil, and filter through a 9 cm quantitative

filter. Repeat the operation twice; transfer the ash completely to the filter paper and wash with three successive portions of hot water; dry and ignite the filter with the undissolved residue at low red heat, cool, weigh, and calculate as insoluble ash. Cool the filtrate and titrate with tenth-normal hydrochloric acid, using methyl orange as indicator. Express results as number of cubic centimeters of tenth-normal hydrochloric acid per 100 cc sample.

13. *Soluble and insoluble phosphoric acid.*—Insert "8. Phosphoric acid of the ash," Bulletin 107, Revised, page 102.

14. *Total acids.*—Insert "9. Total acids," Bulletin 107, Revised, page 103.

15. *Fixed acid.*—Measure 10 cc into a 200 cc porcelain casserole, evaporate just to dryness, add 5 to 10 cc of water and again evaporate; repeat until at least five evaporations have taken place and no odor of acetic acid can be detected. Add nearly 200 cc of recently boiled distilled water and titrate with tenth-normal alkali, using phenolphthalein. One cubic centimeter of tenth-normal alkali is equivalent to 0.0067 gram of malic acid.

16. *Volatile acid.*—Calculate the fixed acid as acetic and deduct from the total acid. Express as acetic acid.

17. *Lead precipitate.*—To 10 cc in a test tube add 2 cc normal lead acetate (20 per cent solution), shake, and let stand one-half hour. Express as turbidity, light, medium, heavy, or very heavy.

18. *Color.*—*Brewer's scale.*—Read in good, reflected daylight, using 0.5-inch cell and the Lovibond scale.

19. *Color removed by fuller's earth.*—To 50 cc add 25 grams of fuller's earth, shake at intervals for 30 minutes and filter through a fluted filter. Put equal volumes of treated and original sample in adjoining colorimetric tubes, make to 50 cc with water, and compare the degrees of color in some form of colorimeter. Express results as per cent of color removed. On account of its varying quality it is necessary for the analyst to standardize the fuller's earth used against vinegars of known purity.

20. *Alcohol precipitate.*—Evaporate 100 cc of vinegar to about 15 cc. It has been observed that when there is considerable sugar in the vinegar if the sample is evaporated to too low a volume, on adding the alcohol a gummy or stringy precipitate occurs instead of a flocculent one. When the sugar content is high, therefore, the evaporation should not be carried beyond 20 cc. To this residue add 200 cc of 95 per cent alcohol slowly and with constant stirring, and allow the mixture to stand overnight. From this point follow the method for determination of alcohol precipitate under "XII. Fruits and fruit products," page 80, Bulletin 107, Revised.

21. *Pentosans.*—Follow the method as given under "VI. General methods," page 54, Bulletin 107, Revised. To 100 cc of vinegar add 43 cc of hydrochloric acid (specific gravity 1.19), and then distil exactly according to directions given.

22. *Heavy metals.*—Insert "23. Heavy metals," Bulletin 107, Revised, page 105.

23. *Detection of preservatives.*—Insert "24. Detection of preservatives," Bulletin 107, Revised, page 105.

REPORT ON FLAVORING EXTRACTS.

By R. S. HILTNER, *Associate Referee.*

PLAN OF WORK.

The plan for cooperative work on this subject for this year was based largely on the recommendations made by the referee and adopted by the association at the last meeting. These recommendations called for the study of the method of determining vanillin, coumarin, and normal lead number in one weighed portion, as proposed by Winton, Lott, and Berry, and the investigation of the Woodman-Newhall test for caramel in vanilla extracts; the study of the La Wall-Nelson tests for capsicum in ginger extracts and of the methods for the examination of nutmeg and wintergreen extracts.

In addition to these investigations that were recommended, it was thought advisable to study some of the more promising methods, bearing directly on

these subjects, that have been published recently. These methods comprised, *first*, a test for caramel in vanilla extracts, using the method described by Tolman (Bul. 132, p. 90) to determine per cent of color insoluble in amyl alcohol (Marsh reagent); *second*, Denis's method for the detection of prune juice and sherry residues in vanilla extracts;¹ *third*, Mitchell's modification of the Seeker test for ginger in alcoholic solutions (see p. 137); *fourth*, Howard's modified general method for the determination of essential oils in alcoholic solutions² applied to nutmeg, wintergreen, and peppermint extracts.

An effort was made to prepare the samples in such a manner that the reliability of each of the methods, under varying conditions, could be ascertained. Sets of samples, with descriptions of the methods to be employed, were sent to the 15 members of the association who had offered to collaborate. More or less complete reports were received from the following chemists:

1. E. H. Berry, Chicago.
2. E. Bloomberg, Galveston.
3. C. S. Brinton, Philadelphia.
4. Courtney Conover, Pittsburgh.
5. Fred F. Flanders, Boston.
6. E. H. Grant, New Orleans.
7. A. W. Hanson, Kansas City.
8. A. M. Henry, Florida State Agricultural Department.
9. M. B. Kennedy, University of Nevada, Reno.
10. F. W. Liepsner, Kansas City.
11. Byron McClelland, New York.
12. E. L. P. Treuthardt, Washington.
13. Burton B. Wilcox, New York.
14. C. O. Dodge, Washington, D. C.
15. R. S. Hiltner, Denver, Colo.

To these chemists the associate referee desires to acknowledge his indebtedness for the data furnished and the interest manifested; also to A. L. Winton for valuable assistance and for the complete report from his laboratory. The names of the analysts have been arranged in alphabetical order and numbered accordingly. To simplify the presentation of the data in tabular form, the analysts will be referred to by number rather than by name.

VANILLA EXTRACTS.

Collaborators were asked to use the following methods in examining the seven samples that were furnished:

METHODS FOR EXAMINATION OF VANILLA EXTRACTS.

Determinations are to be made in one weighed portion of sample.

Special reagents.—Distilled water, boiled until free from carbon dioxid.

Standard lead acetate solution, 80 grams of C. P. crystallized lead acetate dissolved in water and made up to 1 liter.

Ammonium hydroxid solution, containing approximately 2 per cent of ammonia.

Hydrochloric acid solution, containing approximately 10 per cent of hydrochloric acid.

(a) *Vanillin and coumarin.*

(See Winton's paper, p. 147.)

¹ J. Ind. Eng. Chem., 1911, 3: 254.

² J. Ind. Eng. Chem., 1911, 3: 252.

(b) Normal lead number.

(See Winton's paper, p. 148.)

(c) Residual color after precipitation with lead acetate.

(See Winton's paper, p. 148.)

(d) Caramel.

Test each sample for caramel by the Woodman and Newhall method. (See Cir. 66, p. 19.)

(e) Color insoluble in amyl alcohol.

(See Winton's paper, p. 149.)

(f) Prune extract.

Examine the samples for prune juice as directed by Denis (J. Ind. Eng. Chem., 1911, 3:254). Report results as positive or negative.

In each case express an opinion as to whether the sample is a genuine standard vanilla extract U. S. P. In samples that are found not standard state the nature of the adulterant indicated.

DESCRIPTION OF SAMPLES.

The following is a description of the samples that were prepared:

No. 1. Pure vanilla extract made according to the U. S. Pharmacopœia formula, from Bourbon, Seychelles, Comores, and Mexican beans (extract made at the U. S. Food and Drug Inspection Laboratory, Chicago).

No. 2. Vanilla extract (Mexican and Tahiti beans) adulterated with extract of dried prunes, synthetic vanillin, and colored with caramel.

No. 3. Pure vanilla extract, made according to the U. S. P. formula from a good grade of Mexican beans.

No. 4. A wholly factitious product, containing 25 per cent tonka-bean extract (10 per cent tonka beans, 20 per cent sugar, 70 per cent diluted alcohol) and 75 per cent of extract of dried prunes, to which was added enough synthetic vanillin to amount to 0.15 per cent in the finished product. Caramel was used to give the desired color.

No. 5. Pure vanilla extract, made according to the U. S. P. formula from a rather inferior grade of Tahiti beans.

No. 6. Contained about 40 per cent Tahiti-bean extract (No. 5) adulterated with synthetic vanillin so as to yield 0.17 per cent, and with other material to imitate genuine vanilla extract. Caramel was used for color.

No. 7. Commercial vanilla extract made in Denver and warranted by the manufacturer to be pure and according to U. S. standard, from Mexican beans 34 per cent, Bourbon 60 per cent, and Tahiti 6 per cent.

In preparing the factitious samples Nos. 2 and 6 an effort was made to imitate genuine vanilla extracts in the matter of color, vanillin content, lead number, and also to approximate the odor and flavor of the natural product. Sherry residues were not added to any of the samples. It seems inadvisable to make public the exact formulæ used. Members of the association who may be interested in the matter may, of course, secure the information by correspondence.

ANALYTICAL RESULTS.

The results as reported are given in Table 1.

TABLE 1.—*Cooperative work on vanilla extracts.*

Analyst and sample number.	Vanillin.	Con- marin.	Normal lead number.	Residual color in filtrate after precipita- tion with lead acetate.				Color insoluble in Marshall's amyli alcohol reagent.	Caramel, Woodman- Newhall method.	Denis method.		Conclusions as to character of samples.
				Red.	Yellow.	Total color, red and yellow.	Total color, brewer's scale.			Prune juice.	Sherry residue.	
Sample 1.												
1.....	Per cent. 0.19	Per cent. None.	0.57	Per cent. 4.0	Per cent. 6.9	Per cent. 6.1	Per cent. 9.9	Per cent. 23.2	Pos.	Neg.	Neg.	Appears to be straight vanilla extract. Probably pure extract. Genuine vanilla extract. Artificially colored with caramel and sherry residue. Vanilla extract colored with sherry residue.
2.....	.20	None.	.46						Neg.	do.	do.	
3.....	.17	None.	.59					19.0	Doubtful.	do.	do.	
4.....	.19	None.	.54					40.0	Pos.	do.	Pos.	
5.....	.17	None.	.59						Neg.	do.	do.	
6.....	1.10	2 0.63	.63						Neg.	Neg.	Neg.	U. S. P. extract.
7.....	1.21	2.02	.56					16.7	do.	Neg.	Neg.	Straight extract.
8.....	.19	None.	.63					23.0	Neg.	Neg.	Neg.	Denis test indicates genuine vanilla.
9.....	.14	None.	.56	3.0	6.0	5.1	5.7	19.3	do.			
10.....	.18	None.	.52	4.0	5.5							
Sample 2.												
1.....	.17	None.	.42	9.6	14.0	12.8		52.6	Pos.	Pos.	Neg.	Vanillin solution, caramel, and prune juice.
2.....	.17	None.	.34						do.	do.	do.	Probably vanilla extract and prune juice.
3.....								16.9	Doubtful.	do.	do.	Caramel and prune juice indicated.
4.....	.15	None.	.35					54.0	Pos.	do.	do.	Vanillin, caramel, and prune juice added.
5.....	.16	None.	.35					50.0	do.	do.	do.	Vanilla extract colored with prune juice.
6.....	.18	None.	.45						Neg.	do.	do.	
7.....	1.10	2 0.61	.46									
8.....	1.13	2.02	.21					59.5	Pos.	Doubtful.	Neg.	Apparently U. S. P. with caramel.
9.....	.17	None.	.37					10.9	do.			Straight; reinforced.
10.....			.39					55.0	Pos.	Pos.	Neg.	Denis test indicates caramel and prune extract.
11.....	.14	None.	3.44	11.0	18.0			63.1	do.			
12.....	.16	None.	.42	9.1	16.2	14.3	11.6					
Sample 3.												
1.....	.20	None.	.51	3.7	6.2	5.5		23.2	Pos.	Neg.	Neg.	Appears straight vanilla extract.

TABLE 1.—Cooperative work on vanilla extracts—Continued.

Analyst and sample number.	Vanillin.	Con- marin.	Normal lead number.	Residual color in filtrate after precipita- tion with lead acetate.				Color insoluble in Marsh's amyl alcohol reagent.	Caramel, Woodman- Newhall method.	Denis method.		Conclusions as to character of samples.
				Red.	Yellow.	Total color, red and yellow.	Total color, brewer's scale.			Prune juice.	Sherry residue.	
<i>Sample 6.</i>	<i>Per cent.</i>	<i>Per cent.</i>		<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>				
1.....	.16	None.	0.39	15.1	20.2	18.8	26.0	76.9	Pos.....	Neg.....	Neg.....	Vanillin solution and caramel.
2.....	.16	None.	.31						do.....	do.....		Not standard vanilla; probably arti- ficially colored.
3.....									Neg.....	Pos.....	do.....	Caramel and prune juice indicated.
4.....	.15	None.	.40				19.3	70.0	do.....	Neg.....	do.....	Vanilla extract colored with caramel.
8.....								59.0	Pos.....	Neg.....	Neg.....	Apparently U. S. P. with caramel.
9.....	1.08	2 0.013	.47						do.....	Pos.....	Pos.....	Prunes and sherry added.
10.....	1.20	2.008	.38					51.0	Neg.....	Doubtful...	Doubtful...	Denis test gave no positive indications.
11.....	.16	None.	.37				14.4		Pos.....	Neg.....	Neg.....	
12.....			.35						do.....	Pos.....	Pos.....	
13.....	.13	None.	.37	15.0	24.0				Neg.....	Neg.....	Neg.....	
14.....	.15	None.	.38	13.9	22.1	29.8	17.5	60.2	Pos.....	Pos.....	Doubtful...	
<i>Sample 7.</i>												
1.....	.30	None.	.73	3.3	5.4	4.8		26.3	Pos.....	Neg.....	Neg.....	Appears true extract but for high vanil- lin.
2.....	.30	None.	.60				8.0		Neg.....	do.....	do.....	Highly colored dilute vanilla extract.
3.....								23.0	Doubtful...	do.....	do.....	Contains vanillin and prune extract.
4.....	.23	None.	.78				6.6	42.5	do.....	Pos.....	do.....	Vanilla extract, vanillin and sherry residue.
6.....	.36	None.	.71				5.5		Neg.....	Neg.....	Pos.....	
8.....	.32	None.	.89						do.....	do.....	do.....	
9.....	1.15	2 0.041	.77						do.....	do.....	do.....	
10.....	1.31	2.016	.74						Neg.....	Neg.....	Neg.....	Contains added vanillin; not U. S. P.
11.....	.31	None.	.66				5.1	24.5	do.....	Neg.....	Neg.....	Prune; vanilla may be present.
12.....			.72					24.0	Neg.....	Neg.....	Neg.....	Denis test indicates genuine vanilla extract.
14.....	.25	None.	.74	3.0	3.0			25.7	Doubtful...	Neg.....	Neg.....	
15.....	.31	None.	.70	2.7	4.2	4.0	5.3		do.....	do.....	do.....	

¹ Not purified.² Not identified.

Winton has observed that in vanilla extracts the determination of the percentages of colors (red and yellow) of the original extract remaining in the filtrate after precipitation with lead acetate affords valuable information for distinguishing genuine extracts from artificially colored and otherwise adulterated products. The results reported by three analysts are given in Table 1. Further studies have shown Winton that the ratio of red to yellow in the extract and in the filtrate furnishes a still better criterion. The amounts of red and yellow that comprise the composite color of the solution may be determined quite exactly with a Lovibond tintometer, using the standard color glasses. Although it was requested that this method be tried, only three analysts reported on the subject. It seems that very few of the laboratories are equipped with the necessary apparatus, particularly with complete sets of the standard color glasses. In Table 2 are recorded the results of the tests of this method:

TABLE 2.—Comparison of color of vanilla extracts and filtrates.

Analyst and sample numbers.	Color value.				Ratio of red to yellow.	
	Original extract.		Lead acetate filtrate.			
	Red.	Yellow.	Red.	Yellow.	Extract.	Filtrate.
<i>Sample 1.</i>						
1.....	35	100	1.4	6.9	1:2.9	1:4.9
14.....	30	113	1.1	7.0	1:3.8	1:6.5
15.....	35	113	1.4	6.2	1:3.2	1:4.4
<i>Sample 2.</i>						
1.....	50	125	4.8	17.6	1:2.5	1:3.7
14.....	46	170	5.3	32.0	1:3.7	1:6.0
15.....	48	123	4.4	20.0	1:2.5	1:4.5
<i>Sample 3.</i>						
1.....	38	113	1.4	7.0	1:3.0	1:5.0
14.....	29	123	1.5	8.3	1:4.2	1:5.5
15.....	58	258	2.4	12.4	1:4.4	1:5.1
<i>Sample 4.</i>						
1.....	43	85	8.4	30.2	1:2.0	1:3.6
14.....	31	83	7.9	39.0	1:2.7	1:4.9
15.....	39	89	8.6	38.4	1:2.3	1:4.4
<i>Sample 5.</i>						
1.....	40	110	1.4	7.0	1:2.8	1:5.0
14.....	28	122	1.2	7.0	1:4.3	1:5.8
15.....	37	125	1.5	7.2	1:3.4	1:4.8
<i>Sample 6.</i>						
1.....	33	85	5.0	17.2	1:2.6	1:3.4
14.....	29	90	4.3	22.0	1:3.1	1:5.1
15.....	33	85	4.6	18.8	1:2.6	1:4.0
<i>Sample 7.</i>						
1.....	48	133	1.6	7.2	1:2.8	1:4.5
14.....	40	182	1.1	5.8	1:4.5	1:5.8
15.....	48	160	1.3	7.0	1:3.2	1:5.4

As no inch or half-inch cell was available a 50 mm polariscope tube was used. This gave too much color. Readings were reduced to 1-inch cell.

ABSTRACT OF COMMENTS OF ANALYSTS.

E. H. Berry: The Woodman-Newhall test for caramel was tried on three uncolored authentic samples of vanilla and gave positive results on all. In official samples 1, 3, and 5, the Denis test indicated sherry residues. An authentic extract made from Mexican beans gave a similar result, namely, a small amount of light-colored precipitate insoluble in acetic acid. Pure extracts of Bourbon and Tahiti beans gave lead precipitates which dissolved almost completely in the dilute acetic acid reagent.

A. L. Winton: Samples 1, 3, and 5 appear to be straight vanilla extract, and the only thing that leads me to suspect sample No. 7 is the high vanillin. It may be true vanilla extract to which vanillin has been added, although I have known true extracts to go as high as 0.3 per cent, or even, in very exceptional cases, 0.35 per cent. Samples 2 and 6 appear to contain the same substances with the exception of prune juice, which was found to be present in 2, but not in 6. The other constituents, other than vanilla extract, are evidently vanillin solution and caramel, although the evidence of added vanillin is not absolutely conclusive. The samples might be straight vanilla extracts of high vanillin content, merely diluted. This is not, however, probable. Sample No. 4, in addition to vanilla extract, contains either tonka extract or coumarin solution, caramel, and prune juice. In reaching these conclusions I have paid no attention to Woodman and Newhall's test, which we have not found valuable.

The Marsh test appears to corroborate the results obtained on the color values of the extract and of the lead filtrate as followed by us. It has the advantage of direct comparison of the two liquids in a colorimeter, thus eliminating the cumbersome figures for red and yellow required in the other process. On the other hand, it has the disadvantage that another portion of the extract must be taken. Both methods give ambiguous results on two samples of extract made from Ceylon beans in this laboratory. These results appear to be abnormal. In fact, the results in color value and Marsh test are about the same as for your sample No. 2, which appears to contain caramel. These two extracts have perplexed us quite a deal and I have about reached the conclusion that either the beans have been extracted (they contain only 0.07 per cent vanillin) and soaked, say, in caramel solution, or else they represent a very abnormal product, comparable, for example, with cow's milk containing only 2 per cent of fat.

E. Bloomberg: In each case the residue was obtained for coumarin, but only those cases in which a qualitative test showed its presence were reported. The prune juice test seems inconclusive. In every case, excepting No. 6, a residue was obtained after the addition of acetic acid. In Nos. 1 and 7 the residue was yellowish and granular. In Nos. 3 and 5 a considerable yellowish flocculent residue remained. This would seem to indicate the presence of sherry wine coloring.

C. S. Brinton: In the experience of this laboratory (Philadelphia) we do not consider the modified paraldehyde test for caramel entirely satisfactory, unless a dark-brown precipitate, which adheres to the test tube, is obtained. In samples 1, 2, 6, and 7 small amounts of brown flocculent nonadherent precipitate were obtained, and in all four of these samples I believe that caramel is absent. The Denis test for prune juice and sherry residue has been found unreliable. Four pure extracts made according to the U. S. P. formula from Bourbon, Mexican, and South American beans and Mexican "cuts" when subjected to this test gave very inconsistent results. My conclusions as to the character of the seven official samples were based largely on the results of the Woodman-Newhall and Denis tests and must be considered accordingly.

Courtney Conover: Sample No. 1 appears to be a genuine vanilla extract. The other six samples seem abnormal in certain respects. Nos. 2, 3, 4, 6, and 7 respond positively to the test for prune extract. No. 5 gave a somewhat doubtful test for sherry residue. The lead numbers of samples 3, 5, and 7 are very high and apparently confirm the results of the Denis test. The reactions for prune extract, to an inexperienced person, would not be very definite. The Woodman-Newhall test for caramel is somewhat unsatisfactory, except in the presence of large amounts. The improved lead subacetate method for caramel, proposed by Albrech and Conover, gave positive evidence of the presence of caramel in Nos. 2, 4, and 6. Nos. 1, 3, and 5 appeared to be abnormal extracts, possibly colored with a very small amount of caramel or other color. No. 7 seems to contain no caramel.

E. H. Grant: Results indicate that No. 1 is wholly artificial, colored with caramel and sherry residue. Likewise No. 4, except that prune extract is present instead of sherry. In No. 5 the excessively high lead number indicates the addition of foreign substances. It is colored with prune extract. No. 7 is probably fortified with vanillin and colored with prune extract.

F. W. Liepsner: The figures reported for per cent vanillin and coumarin represent the weights of the dried but unpurified ether extracts. The residues weighed as coumarin were not tested qualitatively for that substance. The results therefore must be judged accordingly.

A. M. Henry obtained better results by measuring out at the beginning enough 10 per cent hydrochloric acid into the separatory funnels to neutralize the

ammoniacal solutions of vanillin. This gives very little opportunity for the ammonia to attack the vanillin.

M. B. Kennedy: The figures reported under vanillin and coumarin represent the unpurified, dried residues from the ether extractions. Qualitative tests for coumarin were not made.

DISCUSSION BY THE REFEREE.

For the determination of vanillin, lead number, etc., I would recommend that 50 cc of the sample be used instead of 50 grams, for the reason that the United States standard for vanilla extract requires at least 10 grams of vanilla beans per 100 cc and because the U. S. P. and other formulas specify a certain weight of beans for unit volume of menstruum. Furthermore the specific gravity of solvents used in commercial extracts varies so decidedly that it would seem advisable to measure rather than weigh the sample and obtain results in terms of grams per 100 cc, and thus determine more directly the matter of conformity to the standard.

To insure exact aliquots of the solution for determining vanillin and coumarin and lead number, as directed in paragraphs (a) and (b), it would seem desirable to specify in the text of the method, first, that after adding lead acetate the solution should be warmed to approximately 38° and made up to the mark with water at the same temperature; and, second, that the aliquot portions of the filtrate should be drawn off while the solution is at the incubator temperature. These details would lead to uniformity of results.

The color of the filtrates, after precipitation with lead acetate, by the Winton-Lott-Berry method, usually gives dependable information as to the character of the extracts. In genuine products, irrespective of the nature of the solvent, the color of the filtrate is light straw tint and will seldom exceed 10 units of the brewer's scale, as gauged in a 1-inch cell of a Lovibond tintometer. Except with very artfully adulterated samples this very simple test will suffice to distinguish pure extracts from those artificially colored, especially with caramel.

It seems to be the almost universal experience of analysts that residues of vanillin and coumarin, resulting from the evaporation of ether extracts, are seldom, if ever, pure, but are contaminated with more or less gummy matter. Consequently results from weighing the crude product are usually too high. The error will often amount to 0.04 per cent. If the residues are extracted with petroleum ether by the method suggested and the vanillin and coumarin thus purified, the results are frequently too low, because the resinous or gummy matter, being insoluble in petroleum ether, often prevents complete solution of the vanillin and coumarin, with which it is intimately mixed. At best, the method of purification as prescribed, especially for vanillin, is tedious and exacting and requires skillful manipulation to prevent loss. The results reported for No. 3 emphasize the difficulties the analysts had in determining vanillin. That sample yielded about 0.04 per cent of gasoline-insoluble matter in the crude vanillin residue. To offset these difficulties, the following procedure is suggested:

Draw off the ether extract of vanillin into a dry 100-cc beaker, evaporate the ether, and dry the residue over sulphuric acid as usual; weigh the beaker and contents gross, then heat in an oven at 105° C. for three or four hours, or until constant weight is attained. Finally cool and weigh. Loss in weight indicates vanillin. Follow the same plan with the ether extract of coumarin. If it be desired to determine the purity of the volatile matter, the beaker may be heated cautiously, first on a hot plate and the sublimate condensed on a cool cover glass and afterward identified by melting points and qualitative tests. The beaker and residue should then

be placed in the oven to complete the volatilization. Vanillin and coumarin appear to be completely volatile at 105°, and the gummy matter seems not to suffer change at that temperature. From various kinds of pure vanilla extracts it exhibits uniformly the same characteristics, viz, brown color, insolubility in water and petroleum ether, ready solubility in alcohol and in alkalis, and slight solubility in ether. In view of these peculiarities of solubility, it would seem to be advantageous to use washed ether to extract the vanillin and coumarin from the samples.

Having had little experience with the Woodman-Newhall test for caramel as applied to vanilla extracts, I was unable to distinguish clearly between the artificially colored and pure extracts by this method. Samples 3, 5, and 7, containing no caramel, gave doubtful results. The test with phenylhydrazin seems entirely unreliable.

The Denis test was not very satisfactory. It responded quite positively with the samples containing prune extract, but with samples containing none the results were not strikingly negative, especially with No. 5, which was pure extract made from Tahiti beans. This gave positive reactions for prune juice. I think with practice the analyst would be able to use this method to advantage in many cases.

CONCLUSIONS.

The results as received from the collaborators seem to warrant the following conclusions with reference to vanilla extracts:

(1) That the Winton-Lott-Berry method can be fully relied upon for the determination of vanillin and coumarin when proper precautions are taken to purify the extracted matter.

(2) That the lead number obtained by the use of normal or neutral lead acetate gives a more dependable number or constant than by sub- or basic acetate of lead, for the reason assigned by the authors of the method.

(3) That the percentage of residual color (either total color or component yellow and red tints) in the lead filtrates, as determined by the Winton-Berry method, gives valuable information as to the presence or absence of added color in vanilla extracts. The principal thing now lacking is a schedule of limits for this percentage of color in pure extracts from various kinds of beans. This also applies to the subject of normal lead number.

(4) That the Tolman method for determining color insoluble in amyl alcohol (Marsh reagent) also gives trustworthy information regarding the coloring matter of vanilla extracts. Data for establishing limiting figures are needed here also. It appears possible that it will be necessary for each analyst to prepare his own standards for comparison. The "personal equation" figures largely in these methods involving color values and color comparison.

(5) That the Woodman-Newhall test for caramel in vanilla extracts can not be relied upon for positive results. The method would be of value only for confirmatory tests and for distinguishing caramel from other artificial coloring in the hands of those who have had considerable experience with various grades of extracts.

(6) That the Denis method for detecting prune juice and sherry residue in vanilla extracts is likewise unreliable. Only one analyst reported correctly regarding the character of the seven samples submitted, and he has had much experience lately with vanilla extracts. The results of the Denis test were considered in connection with the other data. This fact forces the conclusion that the Denis method is sound, but that it can be relied upon only by those who keep in practice and have had considerable experience.

GINGER EXTRACTS.

METHODS AND SAMPLES.

Four samples labeled "Ginger extract" were forwarded to the analysts, with descriptions of the methods to be followed in testing for ginger and capsicum. The methods proposed were—

(a) Test each sample for ginger as directed in Circular 66, page 22. Also try Mitchell's modification of the Seeker test as follows:

Evaporate the ether extract as in the Seeker method. Add to the residue 10 or 12 drops of concentrated sulphuric acid and about 5 mg of vanillin. Mix thoroughly by rubbing with a glass rod; then allow a few drops of water to flow down into the mixture from the side of the dish. A persistent dark blue color indicates ginger.

Report results as positive or negative.

(b) Test the samples for capsicum by the La Wall-Nelson method (Circular 66, page 22), observing the precautions suggested by Doyle to prevent loss of capsicum by volatilization, namely, render the sample slightly alkaline with sodium hydroxid before evaporating the alcohol and then slightly acidify with sulphuric acid before the first extraction with ether. The final ether extract of the saponified solution should be washed with water until neutral to litmus and then allowed to evaporate spontaneously.

Report results as positive or negative.

It was especially desired to learn the value of Mitchell's modification of Seeker's test for ginger and to determine whether the details suggested by Miss Doyle would render more sensitive and positive the La Wall-Nelson test for capsicum.

Sample No. 1 was pure standard ginger extract, made according to the U. S. Pharmacopœia formula for tincture of ginger, using 20 grams of powdered ginger (Japan and Cochin) per 100 cc.

Sample No. 2 consisted of U. S. P. ginger extract (made from pulverized Japan ginger), 50 per cent; tincture of capsicum U. S. P., 0.5 per cent; alcohol, 49.5 per cent; colored with caramel.

Sample No. 3 was also adulterated. It contained less ginger and more capsicum (2.5 times as much) than No. 2. Sirup and caramel were added to approximate the total solids and color of standard ginger extract.

Sample No. 4 contained no ginger extract. It consisted of 2.5 per cent U. S. P. tincture of capsicum, mixed with sirup and caramel to approximate the total solids and color of standard ginger extract.

ANALYTICAL RESULTS.

The results as reported by the analysts are given in Table 3.

TABLE 3.—*Cooperative results on ginger extracts.*

Analyst and sample.	Ginger.		Capsicum.	
	Seeker method.	Mitchell method.	La Wall-Doyle method.	Nelson method.
<i>Sample 1.</i>				
1.	Positive...	Positive...	Negative..	Negative.
2.	do.	do.	do.	do.
3.	do.	do.	do.	Do.
4.	do.	do.	do.	Positive.
5.	do.	do.	do.	do.
6.	do.	do.	do.	do.
7.	do.	do.	do.	Negative.
8.	do.	do.	do.	Do.
9.	do.	do.	do.	do.
11.	do.	Positive...	do.	Do.
12.	do.	do.	do.	do.
14.	do.	do.	do.	Do.
15.	do.	do.	do.	Do.

TABLE 3.—*Cooperative results on ginger extracts*—Continued.

Analyst and sample.	Ginger.		Capsicum.	
	Seeker method.	Mitchell method.	La Wall-Doyle method.	Nelson method.
<i>Sample 2.</i>				
1.....	Positive...	Positive...	Negative...	Negative.
2.....	do.....	do.....	Positive...	
3.....	do.....	do.....	do.....	Positive.
4.....	do.....	do.....	Negative...	Negative.
6.....	do.....	do.....	Positive...	
7.....	do.....	do.....	do.....	Do.
8.....	do.....	do.....	do.....	Do.
9.....	do.....	do.....	Negative...	
11.....	do.....	Positive...	Positive...	Positive.
12.....	do.....	do.....	do.....	
14.....	do.....	do.....	do.....	Do.
15.....	do.....	do.....	do.....	Do.
<i>Sample 3.</i>				
1.....	Positive...	Positive...	Positive...	Negative.
2.....	do.....	do.....	do.....	
3.....	do.....	do.....	do.....	Positive.
4.....	do.....	do.....	Negative...	Negative.
6.....	do.....	do.....	Positive...	
7.....	do.....	do.....	do.....	Positive.
8.....	do.....	do.....	do.....	Do.
9.....	do.....	do.....	Negative...	
11.....	do.....	Positive...	Positive...	Do.
12.....	do.....	do.....	do.....	
14.....	do.....	do.....	do.....	Do.
15.....	do.....	do.....	do.....	Do.
<i>Sample 4.</i>				
1.....	Negative...	Negative...	Positive...	Negative.
2.....	do.....	do.....	do.....	
3.....	do.....	do.....	do.....	Positive.
4.....	do.....	do.....	do.....	Negative.
6.....	do.....	do.....	do.....	
7.....	do.....	Positive...	do.....	Positive.
8.....	do.....	Negative...	do.....	Do.
9.....	do.....	do.....	Negative...	
11.....	Doubtful.	Positive...	Positive...	Do.
12.....	Negative...	Negative...	do.....	
14.....	Doubtful.	Positive...	do.....	Do.
15.....	Negative...	Negative...	do.....	Do.

ABSTRACTS OF COMMENTS OF ANALYSTS.

E. Bloomberg: By using Mitchell's method for ginger, allowing the concentrated sulphuric acid, after mixing, to flow onto the side of the dish and then adding a few drops of water to the thin layer of acid mixture, the blue color appears immediately.

C. S. Brinton found that the Mitchell test gave more strikingly positive results than the original Seeker method and therefore recommends that the modified method be adopted by the association. He regards the La Wall-Doyle method for capsicum as more reliable than the Nelson test.

C. Conover: Seeker's test gave better color reactions than Mitchell's modification. The tests for capsicum by the two proposed methods were inconsistent in samples 1 and 4. In No. 4 the La Wall-Doyle test was strongly positive, while, by the Nelson method, capsicum appeared to be absent.

E. H. Grant: With Mitchell's method I found it advisable to mix the residue with sulphuric acid and vanillin by rotating the dish, rather than by rubbing with a glass rod, as the amount of extracted matter is so high as to give a very dark color if the whole of the residue is taken up.

M. B. Kennedy tested the four ginger extract samples for capsicum by the proposed methods but obtained no positive results.

Byron McClelland: The Nelson test for capsicum appears to be not so decisive as the La Wall-Doyle.

E. L. P. Treuthardt: The Mitchell test for ginger gave a more pronounced coloration than the original method. Sample 4 gave a distinct blue color with

the former, but only a faint violet tint, which was not regarded as a positive test, with the Seeker method. For the detection of capsicum the use of manganese dioxid more effectually decomposes the ginger, but it lessens the delicacy of the test for capsicum. The Doyle modification of La Wall's method gives a more positive indication of capsicum than does the Nelson test. In every case where capsicum was reported present, there was a distinct "bite" on the tongue surely due to capsicum. In all the samples there was sufficient ginger left in the capsicum residue to give a positive test by the Seeker-Mitchell method. The samples were evidently made up as follows: No. 1, straight ginger extract; No. 2, ginger extract with trace of capsicum and containing less ginger than No. 1; No. 3, weak ginger extract with slight amount of capsicum; No. 4, trace of ginger and much capsicum.

C. O. Dodge considers the color developed by the Seeker test for ginger to be better described as purple and regards the Mitchell modification as more sensitive than the original method.

DISCUSSION BY REFEREE.

I regard Mitchell's test for ginger as a little more sensitive but not so reliable as the Seeker method. Ether extracts of certain other spices were found to give, by the former method, color reactions (shades of blue and purple) that might be easily confused with the color due to ginger. For example, sample No. 4, which contained no ginger, gave a doubtfully positive test with concentrated acid, but a distinctly negative result with more dilute acid (Seeker method). Other analysts experienced the same difficulty in judging this sample. (See Table 3.) I observed that the purplish color developed in No. 4 by the Mitchell test was very fugitive, and in this respect could be clearly distinguished from reactions of ginger.

As a general rule the odor of the sample, especially after the alcohol has evaporated, is sufficient proof of the presence or absence of ginger.

The details of the test for capsicum, as proposed by Doyle, greatly improve the La Wall method. The test may be made a little more sensitive by allowing the final ether extract to drip slowly from the separatory funnel into a small watch glass and regulating the flow in accord with the evaporation, so as to have only a few drops of liquid in the dish at a time, thus restricting the residue to a small area. Determine taste by holding the residue in the watch glass against the tip of the tongue for about a half minute. A hot, stinging sensation distinguishes capsicum and is not easily confused with the mild, warm taste due to traces of ginger.

My experience was in accord with Mr. Treuthardt's with samples 1, 2, and 3, namely, that the residue to be tasted for capsicum (La Wall-Doyle test) gave positive test for ginger by the Seeker method, indicating that conclusions as to traces of capsicum must not be hastily drawn.

Nelson's modification proved unsatisfactory.

NUTMEG EXTRACTS.

The reliability of two methods for determining the percentage of oil of nutmeg in alcoholic solution was tested this year: (A) The A. O. A. C. method for lemon oil in extracts, as given in Bulletin 107, Revised, page 160. Since oil of nutmeg appears to be insoluble in dilute alcohol, and since it is of lower specific gravity than water, this method seemed to be directly applicable. (B) Howard's method as published in *J. Ind. Eng. Chem.*, 1911, 3:252. Following is an outline of the method:

Mix 20 cc of the sample in a separatory funnel with 50 cc of water and 2 drops of hydrochloric acid. Extract the separated oil with three portions of ether and transfer the extract, after washing once with water, to a Babcock milk flask. Rapidly evaporate the ether by immersing the flask, previously

connected to an exhaust pump, in hot water, shaking at first gently and then violently. Finally, float the residual oil on cold water, whirl in a centrifuge, and measure. It was suggested that a thermometer of small diameter be inserted in the neck of the Babcock flask when expelling the ether to control the evaporation and prevent loss of oil. A sharp rise of temperature indicates complete expulsion of ether vapor.¹

Two samples were forwarded to each analyst. Sample No. 1 contained 1.5 per cent and No. 2, 2.5 per cent by volume of oil of nutmeg.

In Table 4 are given the results as reported:

TABLE 4.—*Cooperative results in nutmeg oil in nutmeg extracts.*

Analyst.	Sample No. 1.		Sample No. 2.	
	Method A.	Method B.	Method A.	Method B.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
1	0.7	0.8	1.7	1.8
2	.6	1.1	1.4	2.1
3	1.0	1.9	1.9	2.9
4	.6	.8	1.4	2.0
6	.7	1.0	1.7	1.8
7	.8	.7	1.6	1.6
8	.9	-----	1.8	1.6
12	1.0	1.4	2.0	2.6
13	1.1	1.6	2.0	2.6
14	-----	1.3	-----	-----
15	1.0	.8	1.8	1.6

Three determinations reported, namely, 3.95, 2.90, and 2.85.

ABSTRACTS OF COMMENTS OF ANALYSTS.

E. Bloomberg: Method A gives low results. An attempt was made to separate more of the oil by cooling the precipitated oil and then centrifuging. In this way No. 1 gave 1 per cent of oil and No. 2, 1.7 per cent. The precipitated oil was allowed to remain overnight at room temperature in the flask, securely corked, and then centrifuged. This method gave 1.0 per cent for No. 1 and 1.9 per cent for No. 2. Howard's method seems to offer several chances for loss of oil, owing to the solubility of the oil in the dilute alcohol, and also to the solubility of ether in the dilute alcohol, which, doubtless, carries some oil with it.

C. Conover: The use of a thermometer to control the evaporation in the Howard method seems unnecessary, the rise of temperature being immediately noticeable by the warming up of the Babcock bottle in the hand.

B. B. Wilcox: Results by Method A are too low, because of the solubility of the oil in dilute alcohol. By using 10 cc of the extract instead of 20 cc this difficulty was in some measure removed. The effect of the error in reading is, of course, doubled. It seems probable that by using a Babcock bottle of 100 cc or more capacity, and using 20 cc of the sample, results of some accuracy could be obtained. Repeated tests of Howard's methods with extracts of known strengths failed to give the true amounts of oil or concordant results. The difficulty seemed to be in some cases that the ether was not completely removed and in others that some oil was volatilized.

E. L. P. Treuthardt: In methods such as these, where the volume of the separated oil is measured, it is important that points at which the column of oil is to be read should be clearly stated. My experience indicates that the extreme points should always be the ones noted.

C. O. Dodge: The alcohol of these samples is very much stronger than is necessary to hold the oil in solution. Method A could be applied only after a preliminary dilution and the multiplication of errors renders the results valueless.

REFEREE'S DISCUSSION AND CONCLUSIONS.

I was unable to obtain either accurate or concordant results with the methods proposed or, in fact, with any modifications that suggested themselves. The

¹ Method offered by C. O. Dodge, Bureau of Chemistry, Washington, D. C.

principal difficulty experienced with the Howard method was that part of the extracted oil, after evaporating the ether, collected in small globules on the walls of the bottles and resisted every effort to dislodge them by mechanical means. My observations accord exactly with those noted by Mr. Wilcox.

Considering the results and comments of the 11 analysts who reported on these samples, it is apparent that the methods tried this year for determining oil of nutmeg in alcoholic solutions are of no value. Moreover, it appears that simple modifications of the methods fail to give reliable results. No analyst reported correctly the amount of oil present. The difficulty with Howard's method, as Mr. Wilcox states, seems to be that either the oil is partly volatilized giving low results or the ether is not completely removed giving high results.

As noted by Mr. Dodge, the alcohol used in preparing the samples of nutmeg, wintergreen, and peppermint extracts was of unnecessarily high proof. This strong alcohol was used for the purpose of testing the reliability of the method under extreme conditions.

WINTERGREEN EXTRACTS.

METHODS AND ANALYTICAL RESULTS.

Three methods were proposed for determining the percentage of oil of wintergreen in alcoholic solutions:

(A) Howard's method, (*J. Ind. Eng. Chem.*, 1911, 3: p. 252), using cold sulphuric acid (1:2) for the floating medium. This method is the same as for oil in nutmeg extracts, as described above, except that dilute sulphuric acid is used to float the oil owing to the high specific gravity of oil of wintergreen.

(B) A modification of Hortvet and West's method.

Method B.—Pipette 50 cc of the sample into a separatory funnel, add 5 drops concentrated hydrochloric acid and 125 cc cold water. Shake out with three portions of ether, 30 cc, 20 cc, and 10 cc, respectively; wash with ether-saturated water as directed by Howard (*supra*); then transfer the ether extract to a Hortvet tube (as used for lead precipitate in maple products). Evaporate the bulk of the ether by aspirating cold through a two-hole cork, using one hole for a vent. Immerse the tube in boiling water and proceed according to Howard's method until the ether is eliminated. Finally add 15 cc hot water, centrifuge and measure the oil at room temperature.

This is a modification of Hortvet and West's method¹ as regards the apparatus used. It appeared feasible to use in this way the well-known Hortvet (lead precipitate) tubes, and thus obviate the necessity of special apparatus.

(C) Hortvet and West's method of saponifying the oil and weighing as salicylic acid. (*J. Ind. Eng. Chem.*, 1909, 1:90.) The following is an abstract of this method:

Mix 10 cc of the extract with 10 cc of potassium hydroxid solution (10 per cent). Heat on the steam bath until the volume is reduced about one-half. Add a distinct excess of dilute hydrochloric acid; cool and extract with three portions of ether, 40 cc, 30 cc, and 20 cc, respectively. Filter the extract through a dry filter into a weighed dish, wash with 10 cc ether and allow to evaporate spontaneously. Dry over sulphuric acid in a desiccator, weigh, and calculate by the formula: Weight salicylic acid $\times 9.33$ = per cent oil of wintergreen by volume.

Two samples were prepared. Sample No. 1 contained 2.5 per cent, and No. 2, 3.0 per cent of oil of wintergreen (natural) dissolved in 95 per cent alcohol. The results are given in Table 5.

¹ *J. Ind. Eng. Chem.* 1909, 1:90.

TABLE 5.—*Cooperative results on oil of wintergreen in wintergreen extracts.*

Analyst.	Sample No. 1.			Sample No. 2.		
	Method A.	Method B.	Method C.	Method A.	Method B.	Method C.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
1	2.5	2.6	2.48	3.2	3.2	2.95
2	2.9	3.0	-----	3.4	3.3	-----
3	¹ 2.9	-----	-----	¹ 4.2	-----	-----
4	2.3	2.6	2.50	2.7	3.2	3.00
5	3.8	3.6	2.53	3.7	3.8	2.97
6	2.5	-----	2.47	3.0	-----	2.98
7	2.4	2.5	2.39	3.1	3.2	2.98
8	2.8	2.2	-----	5.4	3.0	-----
12	2.5	2.6	3.50	3.1	3.1	4.20
13	-----	-----	2.64	-----	-----	3.24
14	2.5	-----	2.49	3.0	-----	2.99
15	2.5	2.2	2.46	3.0	2.8	2.98

¹ Analyst No. 3 reported sample No. 1, 2.85 and 6.25 and sample No. 2, 4.2 and 5.2.

ABSTRACTS OF COMMENTS OF ANALYSTS.

E. H. Berry: In Method B it was very difficult to remove all the ether.

C. Conover considers Method C, by saponification, to be very satisfactory.

B. B. Wilcox: The observations concerning Howard's method for nutmeg oil apply also to the determinations of oil of wintergreen and peppermint. Method B being similar to Howard's method was not tried.

C. O. Dodge: In Method B the evaporation from the Hortvet tube is extremely difficult owing to spurling. With Method C, I found that drying one hour in a desiccator, as specified, was not sufficient with the large amount of salicylic acid present.

R. S. Hiltner: Methods A and C proved very satisfactory in every particular. With Method A loss of oil by volatilization does not occur. Method B seems to have no special merit.

CONCLUSIONS.

For determining oil of wintergreen in alcoholic solutions, both the Howard method of extracting with ether and floating the extracted oil on dilute sulphuric acid and the Hortvet-West method of saponification of the oil and weighing as salicylic acid, gave satisfactory results, except in two or three cases. It would seem advisable to have both methods adopted by the association for counter-checking results. Method B failed to give accurate results and, having no special points of merit, need not be further considered by the association.

PEPPERMINT EXTRACTS.

METHODS AND RESULTS.

Cooperation was asked on two methods for the determination of oil of peppermint in alcoholic solutions:

(A) The same procedure as for lemon oil in lemon extract as given in Bulletin 107, Revised, page 160.

(B) Howard's method (*J. Ind. Eng. Chem.*, 1911, 3: p. 252) observing the precaution suggested by Dodge to prevent evaporation of the oil, and using salt solution instead of cold water to float the oil. This method is the same as for nutmeg extracts (see p. 139), and appeared to be the most promising of any that had been proposed. It is a slight modification by the author of the original method, which the association adopted provisionally last year. The use of chloroform is omitted.

Two samples of peppermint extract were sent to the analysts. Sample No. 1 contained 2.5 per cent and sample No. 2, 3.25 per cent by volume of oil of peppermint (American), dissolved in alcohol. The results as reported are given in Table 6.

TABLE 6.—*Cooperative results on oil of peppermint in peppermint extracts.*

Analyst.	Sample No. 1.		Sample No. 2.	
	Method A.	Method B.	Method A.	Method B.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
1	0.5	2.4	0.8	3.4
2	.8	3.4	1.1	4.9
3	.8	3.5	1.6	5.1
4	.5	2.5	.9	3.8
5	.2	7.1	.8	6.8
7	.5	2.4	1.2	3.2
8	.6	2.4	.9	-----
12	.8	2.6	1.2	3.7
13	.5	2.0	1.1	2.7
14	2.1	3.1	-----	-----
15	.8	2.4	1.5	3.0

ABSTRACTS OF COMMENTS OF ANALYSTS.

E. H. Berry: Method A has been generally recognized as valueless for use with peppermint extracts. The oil does not all precipitate.

E. Bloomberg: My comments on the methods for nutmeg apply with even greater force to the determination of oil of peppermint, because it is more soluble in dilute alcohol than oil of nutmeg. The same variations were tried with peppermint. On cooling and centrifuging No. 1 gave 1.4 and No. 2, 2.2 per cent. On allowing to stand overnight No. 1 gave 1.5 and No. 2, 2.6 per cent of oil.

E. H. Grant: Results on peppermint extract were very unsatisfactory. The exact difficulty is not apparent. With the association method the oil seemed to be quite soluble in the diluted sample. No. 1 yielded 2.9 per cent oil by Howard's method.

B. B. Wilcox: By using 10 cc of the sample instead of 22 cc in Method A, I obtained 2 and 2.7 per cent of oil, respectively, in Nos. 1 and 2.

CONCLUSIONS.

The methods tried this year for the determination of oil of peppermint are not to be relied upon. The precipitation method, corresponding to the association method for lemon oil, proved utterly worthless. Howard's method gave better results, but was far from satisfactory. A comparison of the percentages of oil present in the samples with the amounts reported in Table 6 will show how unreliable the methods proved.

RECOMMENDATIONS.

Summing up the work of the year, it appears that considerable progress has been made. The methods now at hand will enable the analyst to distinguish with certainty pure vanilla extracts. It may not be possible in every case to determine the exact composition of a factitious sample, but it will be feasible to report positively that such samples are adulterated.

Almost as much may be said of the methods for ginger. There is need, however, of a reliable method for the examination of ginger solids.

There is evident necessity also for better methods for determining essential oils in alcoholic solutions. This is especially true of oil of peppermint. "Ex-

tracts," "essences," and "tinctures" of peppermint, containing such varying amounts of oil in alcohol of high proof and low, are important articles of commerce and demand the attention of the food inspection chemist. Reliable methods are desired in this connection to check the growing practice of substituting oil from which menthol has been partially abstracted.

The two methods that have been proposed for the determination of oil of wintergreen in alcohol solutions seem worthy of adoption by the association without further study.

It is recommended—

(1) That the method of determining vanillin, coumarin, normal lead number, and residual color in one weighed portion, as proposed by Winton, Lott, and Berry, be provisionally adopted. In harmony with this recommendation, it is necessary to ask that recommendation No. 2 as adopted last year (Bul. 137, p. 120) be set aside and that the text of the method as given on page 128 (modified as suggested below) be substituted for all material under the heading No. 4, in Bulletin 107, Revised, pages 156 to 158, "4. Determination of vanillin, coumarin, normal lead number, and residual color." These determinations are all to be made in one weighed portion.

On account of the importance of this method as a means of distinguishing between genuine and imitation vanilla extracts, and in view of numerous changes of detail of procedure that have been suggested and that seem worthy of consideration, I ask that a committee, with Dr. Winton as chairman, be appointed at the forthcoming meeting of the association to consider the data of the analysts' reports of this year and the suggestions that have been made, and to draft a text for the method that will be fully in accord with the latest investigations of the subject. The findings of this committee should be accepted by the association as final for the provisional method for determining vanillin, coumarin, lead number, and residual color. In this way much valuable time and work may be saved.

(2) That the above method for determining vanillin, coumarin, normal lead number, and residual color in filtrate, in one weighed portion of sample, be further studied next year for the special purpose of ascertaining the limits of composition of standard vanilla extracts.

(3) That Tolman's method for determining per cent of color insoluble in amyl alcohol (Marsh reagent) be adopted as provisional, and that the text of the method as published in the Proceedings of the association (Bul. 132, p. 90) be inserted as (c) under "11. Test for coloring matter," in Methods of Analysis (Bul. 107, Rev., p. 159). It is further recommended that this method be studied next year for the purpose of determining the range of values for pure vanilla extracts.

(4) That the methods for the determination of benzaldehyde in almond extract be further studied, with the view of determining the reliability of the methods and also the conditions under which aldehyde is oxidized to benzoic acid in commercial extracts, as well as the extent of such oxidation.

(5) That Mitchell's modification of the Seeker test for ginger be adopted as provisional and added to paragraph 3 under "Ginger extract," as an optional or confirmatory test. The description of this test is as follows:

Extract the dealcoholized sample and evaporate the ether as in the Seeker method. Add to the residue 10 or 12 drops of concentrated sulphuric acid and about 5 mg of vanillin. Mix thoroughly by rubbing with a glass rod; then allow a few drops of water to flow down into the mixture from the side of the dish. An azure blue color indicates ginger.

(6) That the method for the detection of capsicum in ginger extract, as proposed by Miss Doyle, modifying the La Wall method, be adopted as provisional. The Doyle method is not essentially different from La Wall's. The details of procedure, however, are such as to make the test more positive and are set forth more clearly than in the latter method. The following is a condensed statement of the method:

To 10 cc of the extract cautiously add dilute sodium hydroxid until the solution reacts very slightly alkaline with litmus paper. Evaporate at about 70° C. to about one-quarter of the original volume, render slightly acid with dilute sulphuric acid, testing with litmus paper. Transfer to a separatory funnel, rinsing the evaporating dish with water, and extract with an equal volume of ether. Avoid emulsification, shaking the funnel gently for a minute or two. Draw off the lower layer and wash the ether extract once with about 10 cc of water. Transfer the washed ether extract to a small evaporating dish, render decidedly alkaline with alcoholic KOH, and evaporate at about 70° until the residue is pasty; then add about 20 cc more of N/2 alcoholic potash and allow to stand on a steam bath until the gingerol is completely saponified. Usually about one-half hour is required. Dissolve the residue in a little water and transfer with water to a small separatory funnel. The volume should not exceed 50 cc. Extract the alkaline solution with an equal volume of ether. Wash the ether extract repeatedly with small amounts of water until no alkaline reaction with litmus is given. Transfer the washed extract to a small evaporating dish, allowing the ether to evaporate spontaneously. Finally, test the residue for capsicum by moistening the tip of the finger, rubbing it around on the bottom and sides of the dish and then applying the finger to the end of the tongue. A hot, stinging or prickly sensation, which persists for several minutes, indicates capsicum.

(7) That the Street-Morrison method (Bul. 137, p. 76) and other available methods for examining and identifying the components of the total solids of ginger extracts be a subject for study next year. Such a method is necessary for proving adulteration in alcoholic extracts of ginger.

(8) That the subject of the determination of oil of nutmeg in nutmeg extract be studied further, and that other methods be tried next year. Both of the methods tried this year proved utterly unreliable.

(9) That, for the determination of oil of wintergreen in wintergreen extracts, both of the following methods be adopted provisionally.

First, Howard's method as described in J. Ind. Eng. Chem., 1911, 3:252, using cold dilute sulphuric acid (1:2) for the floating medium.

Second, Hortvet and West's method of saponifying the oil and weighing as salicylic acid (J. Ind. Eng. Chem., 1909, 1:90).

By the first method the volume of the extracted oil is measured in the stem of a Babcock flask.

By the second method the amount of oil present is found by determining the principal ingredient, viz, methyl salicylate, which constitutes about 99 per cent of oil of wintergreen. Since these methods are based on entirely different principles, they afford a valuable means of checking results.

(10) That the Howard method for the determination of oil of peppermint in alcoholic solutions, which was adopted provisionally last year, be abandoned, and that the subject be given further study. The original method proposed by Howard, which was adopted last year (Bul. 137, p. 76), was modified, in the interests of greater accuracy, by its author, and the new method published in J. Ind. Eng. Chem., 1911, 3:252. The new method was tried this year by eight collaborating chemists. The results reported were quite unsatisfactory, lacking both accuracy and uniformity.

THE CHEMICAL COMPOSITION OF AUTHENTIC VANILLA EXTRACTS, TOGETHER WITH ANALYTICAL METHODS AND LIMITS OF CON- STANTS.

By A. L. WINTON and E. H. BERRY.

VARIATION IN COMPOSITION OF VANILLA EXTRACT.

Standard vanilla extract, as recognized by the food analyst, the pharmacist, and the reputable manufacturer, is a definite product in that it contains in 100 cc of the solution the alcohol-soluble materials from 10 grams of vanilla beans; it is indefinite in that it is more or less variable in its composition, owing partly to variations in the percentages of moisture and soluble constituents of the bean and partly to differences in the methods of extraction. The quality of the extract is also variable, being dependent on the variety and grade of bean, but with our present knowledge this can not be definitely correlated with differences in composition.

The purpose of this paper is to show the variation in composition of extracts made in the laboratory from different varieties, grades, and lengths of vanilla beans and by the use of different menstrua, thus furnishing data to aid in distinguishing between the genuine product and imitations. The methods of analysis, some of which have been developed by the writers, are also described in detail.

VARIETIES OF VANILLA BEANS.

The vanilla bean is a native of Mexico, from which country the finest grades are still obtained. Mexican vanilla is largely consumed in the United States. The product chiefly used in Europe is collectively known as Bourbon vanilla, which includes true Bourbon (the product of Réunion), Seychelles, Comores, Madagascar, etc. Vanilla of somewhat less commercial value and of relatively small importance is produced in South America, Java, and Ceylon. The vanilla of Tahiti has long been recognized as of inferior flavoring value and has commanded a correspondingly low price.

The following quotations per pound, which obtained at the time the samples for this investigation were purchased (August, 1909), show the relative commercial value of the several varieties: Mexican, \$2.50 to \$5; Bourbon (including Comores, Seychelles, and Madagascar), \$2.50 to \$3.25; South American, \$2.50 to \$3; Java, \$2.50; Ceylon, \$2.40; Tahiti, \$0.80.

Vanillons, also known as pompona or La Guayra vanilla, being the fruit of a different species (*Vanilla pompona*) is not true vanilla, and an extract prepared from it is not vanilla extract. These beans are distinguished from genuine vanilla by their shorter length and greater breadth. They are used chiefly in the preparation of sachet powder.

Most of the commercial varieties of beans can be distinguished only by an expert, as the differences are slight and hardly describable. Tahiti beans, however, have in the past been strikingly different from the others, owing to their high moisture content and greasy appearance, and extracts prepared from these beans have been characterized by their light color and characteristic inferior flavor. These defects, however, will doubtless be largely obviated owing to the enforcement of a law which went into effect in French Oceania during the present year, prohibiting the exportation of beans which have not been officially inspected and passed by a board of examiners.

The Tonka bean, which is a true bean in that it is the seed of a legume, as distinguished from the so-called vanilla bean, which is the fruit of an orchid,

has little in common with the latter. The extract from this bean contains coumarin but no vanillin, and has a low color value and low normal lead number.

PROCESSES OF MANUFACTURE OF VANILLA EXTRACT.

The U. S. P. process, which is regarded as standard, is not generally used by manufacturers of vanilla extracts other than pharmacists. Many consider that 50 or even 45 per cent alcohol is quite as efficient as the 60 per cent of the U. S. P. formula, and some substitute glycerin for sugar, for the reason that it is said to retain the flavor better in cooking. The use of alcohol of greater dilution than 45 per cent is impracticable, because it extracts from the beans gelatinous constituents which render percolation difficult or impossible. Alcohol alone, without either sugar or glycerin, is an efficient solvent, but the product is not as salable, owing to the prejudice of the consumer, who is accustomed to the sweet taste.

The time of extraction and of percolation varies in different factories. Most manufacturers soak their beans with alcohol for days and even months before percolation. The U. S. P. process is probably the least efficient of all the commercial processes unless care is taken to use for the menstruum alcohol which has been previously macerated with or percolated through the residue from the extraction of a previous lot of beans; consequently, tentative standards of composition based on the analyses of U. S. P. extracts are not unfavorable to the manufacturer who might employ a more complete method of extraction. The coloring matter of the bean, which is highly prized in the extract, is particularly slow of extraction.

METHODS FOR THE ANALYSIS OF VANILLA EXTRACT.

DETERMINATION OF VANILLIN AND COUMARIN.

*Modified Hess and Prescott method.*¹—Pipette 50 cc of the extract directly into a tared 250 cc beaker with marks showing volumes of 80 and 50 cc; dilute to 80 cc, and evaporate to 50 cc in a water bath kept at 70° C. Dilute again to 80 cc with water and evaporate to 50 cc. Transfer to a 100 cc flask, rinsing the beaker with hot water, add 25 cc of standard lead acetate solution (80 grams of chemically pure crystallized lead acetate, made up to 1 liter), make up to the mark with water, shake and allow to stand 18 hours at a temperature of from 37 to 40° C. in a bacteriological incubator, in a water bath provided with a thermostat, or in any other suitable apparatus. Filter through a small dry filter and pipette off 50 cc of the filtrate into a separatory funnel.

If a determination of normal lead number is desired, pipette off 10 cc of the filtrate into a beaker and proceed as described on page 148. In the latter case, the water used throughout the process should be boiled until free from carbon dioxide. If coloring with caramel is suspected, determine the color value of the original extract and the filtrate (page 148).

To the 50 cc of the filtrate in the separatory funnel add 20 cc of ether and shake. Draw off carefully the aqueous liquid, together with any ether emulsion, and then remove the clear ether solution to another separatory funnel. Repeat the shaking of the aqueous liquid with ether three times, using 15 cc each time.

Shake the combined ether solutions four or five times with 2 per cent ammonium hydroxid, using 10 cc for the first shaking and 5 cc for each subsequent shaking. In drawing off the ammoniacal solution, care should be taken not to allow any of the ether solution to pass through with it. Reserve the ammoniacal solution for the determination of vanillin.

Transfer the ether solution to a weighed dish and allow the ether to evaporate at room temperature. Dry in a sulphuric acid desiccator and weigh. If the residue is pure coumarin, it should have a melting point of 67° C., respond

¹J. Amer. Chem. Soc., 1899, 21: 256; *ibid.*, 1902, 24: 1128; *ibid.*, 1905, 27: 719; U. S. Dept. Agr., Bureau of Chemistry Bul. 132, p. 109, and Bul. 137, p. 120.

to the Leach test, and be completely soluble in three or four portions of petroleum ether (boiling point 30° to 40° C.), stirring with each portion 15 minutes.

Add to the ammoniacal solution 10 per cent hydrochloric acid to slightly acid reaction. This should be done without delay, as the ammoniacal solution on standing grows slowly darker with a loss of vanillin. Cool, and shake out in a separatory funnel with four portions of ether, as described for the first ether extraction. Evaporate the ether solution at room temperature in a weighed dish, dry over sulphuric acid, and weigh. The residue should be pure vanillin, free from any appreciable amount of color and with a melting point of 80° C.

DETERMINATION OF NORMAL LEAD NUMBER.

*Winton and Lott method.*¹—Mix the 10 cc aliquot of the filtrate from the lead acetate precipitate obtained in the determination of vanillin and coumarin (page 147), with 25 cc of water, boiled until free from carbon dioxid, and a moderate excess of sulphuric acid. Add 100 cc of 95 per cent alcohol and mix again. Let stand overnight, filter on a Gooch crucible, wash with 95 per cent alcohol, dry at a moderate heat, ignite at low redness for three minutes, taking care to avoid the reducing flame, and weigh. The normal lead number is calculated by the following formula:

$$P = \frac{100 \times 0.6831(S - W)}{5} = 13.662(S - W)$$

in which P=normal lead number, S=grams of lead sulphate corresponding to 2.5 cc of the standard lead acetate solution as determined in blank analyses, and W=grams of lead sulphate obtained in 10 cc of the filtrate from the lead acetate precipitate as above described.

The standard of the lead acetate solution as determined by blank analyses does not change appreciably on standing; it should, however, be checked from time to time, especially if the bottle is opened frequently, thus permitting absorption of carbon dioxid.

In all steps of the process only water free from carbon dioxid should be used.

DETERMINATION OF COLOR VALUE OF THE EXTRACT.

Pipette 2 cc of the extract into a 50 cc graduated flask and make up to the mark with a mixture of equal parts of 95 per cent alcohol and water. Determine the color value of this diluted extract in terms of red and yellow by means of a Lovibond tintometer, using the 1-inch cell. To obtain the color value of the original extract, multiply the figures for each color by 25.

For example, a reading of 0.6 red and 2.1 yellow obtained on the diluted extract corresponds to a color value of 15 red and 52 yellow calculated to the original extract.

DETERMINATION OF RESIDUAL COLOR AFTER PRECIPITATION WITH LEAD ACETATE.

Determine the color value, in terms of red and yellow, of the filtrate from the lead acetate precipitate, obtained in the determination of "vanillin and coumarin" (p. 147), using the 1-inch Lovibond cell. Multiply the reading by 2, thus reducing the results to the basis of the original extract.

In case the actual reading of the solution is greater than 5 red and 15 yellow, as may happen if the extract is highly colored with caramel, the one-half or one-quarter inch cell should be employed and the readings multiplied respectively by 4 or by 8.

Divide the figures for red and yellow respectively by the corresponding figures of the original extract and multiply the quotients by 100, thus obtaining the percentages of the two colors remaining in the lead acetate filtrate.

For example, if the color value of the original extract is 15 red and 52 yellow and the color value of the lead acetate filtrate, also measured in the 1-inch cell, is 0.6 red and 2.4 yellow, then the residual color after precipitation with lead acetate calculated to the basis of the original extract is 1.2 red and 4.8 yellow or 8 per cent of the red and 9.2 per cent of the yellow.

Calculate also the ratio of red to yellow in both extract and lead filtrate.

¹ U. S. Dept. Agr., Bureau of Chemistry Bul. 132, p. 110, and Bul. 137, p. 120.

DETERMINATION OF COLOR INSOLUBLE IN AMYL ALCOHOL.¹

Marsh test.—Evaporate 25 cc of the extract until the odor of alcohol is no longer apparent and the liquid is reduced to a thick sirup. Dissolve the residue in water and alcohol, using 26.3 cc of 95 per cent alcohol, and making up to volume in a 50 cc flask with water. Transfer 25 cc of this solution to a separatory funnel; add 25 cc of the Marsh reagent and shake, not too vigorously, to avoid emulsification. Allow the layers to separate and repeat the shaking twice more. After the layers have separated clearly, run off the lower layer into a 25 cc cylinder, and make up to volume with 50 per cent by volume alcohol. Filter if necessary and compare in a colorimeter with the remaining 25 cc portion (which has not been extracted with the reagent) and express the results as per cent of color insoluble in amyl alcohol.

The Marsh reagent is prepared as follows:

Mix 100 cc of amyl alcohol, 3 cc of sirupy phosphoric acid, and 3 cc of water; shake before using. If the reagent becomes colored on standing, the amyl alcohol should be redistilled over 5 per cent phosphoric acid.

U. S. P. VANILLA EXTRACTS MADE IN THE LABORATORY.

In order to learn the influence of variety, grade, and length of bean on the composition of vanilla extract, 74 samples were obtained from one of the leading importers. The number of grades of each variety represented were as follows: Mexican, 5; Bourbon, 5; Seychelles, 3; Madagascar, 3; Comores, 4; South American, 3; Ceylon, 1; Java, 1; Tahiti, 1. Whenever possible, two or three lengths of each grade were secured and separate extracts made of each. In addition, one sample each of Mexican cuts and splits, also one of Bourbon splits, were included. One sample of Vanillons and two of Angostura Tonka beans, one "prime" and the other "bloaters," were secured.

Determinations of moisture were made only in the case of one sample of Tahiti beans, which was found to contain 50.53 per cent. Probably none of the samples contained less than 25 per cent of moisture, and none, except the Tahiti samples, as high as 50 per cent. As regards this point they represented fairly the commercial product, which is stated not to change appreciably in moisture content during storage in the tin boxes used for the purpose.

PREPARATION OF EXTRACTS.

The method employed was that for *tinctura vanillæ* (tincture of vanilla) as described in the United States Pharmacopœia, eighth revision, page 484, as follows:

Vanilla, cut into small pieces and bruised, 100 grams; sugar, in coarse powder, 200 grams; and alcohol and water, each a sufficient quantity to make 1,000 cc.

Mix 650 cc of alcohol with 350 cc of water. Macerate the vanilla in 500 cc of the mixture for 12 hours; then drain off the liquid and set it aside. Transfer the vanilla to a mortar, beat it with the sugar into a uniform powder, then pack it in a percolator and pour upon it the reserved liquid. When this has disappeared from the surface, continue the percolation by gradually pouring on sufficient menstruum to make 1,000 cc of tincture.

In all cases, wherever the quantity of the material would permit, 200 grams of the beans and proportionate quantities of the other ingredients were employed. The vanilla, preparatory to extraction, was ground as finely as possible in a meat chopper. The maceration of the ground vanilla was carried on, as directed, for 12 hours, while the percolation, after grinding the residue with the sugar, consumed approximately 12 additional hours.

¹ The method is that employed by Tolman and Hillyer (Bul. 122, p. 206; Bul. 132, p. 90) for the detection of caramel in whisky. The application of this process to the examination of vanilla extract was first suggested by Hiltner.

EXTRACTS FROM RESIDUES OF FIRST EXTRACTION.

The residues from the U. S. P. extractions, representing 200 grams of the beans, were macerated with 500 cc of 60 per cent (by volume) alcohol for five months in glass-stoppered bottles. At the end of that time the contents of the bottle were transferred to a percolator, and after the liquid had run through, fresh portions of 60 per cent alcohol were added until the percolate measured 1 liter.

This liter of second extract accordingly corresponded to the 2 liters of the first extract, but in calculating the analytical results, all of the figures were reduced to the same basis as that of the first extract.

The total percentage of vanillin in the bean may be accurately obtained by adding the figures obtained in the two extracts and multiplying by 10. The totals for normal lead number and color value may also be calculated, but these figures are less significant, as they represent merely what was obtained by the solvents and methods of extraction employed.

RESULTS OF ANALYSES.

In Table 1 are given the detailed results of the analyses of the U. S. P. extracts, together with the maximum, minimum, and average results of the analyses of the extracts made from each variety of beans, as well as of all of the analyses, excluding Ceylon vanilla, Vanillons, and Tonka beans.

The detailed results of the analyses of the extracts prepared from the residues from the U. S. P. extracts, together with the maximum, minimum, and average figures, excluding the varieties noted in the last paragraph, appear in Table 2.

TABLE 1.—*Analyses of vanilla extracts (tincture of vanilla U. S. P.) made in the laboratory.*

Serial No.	Kind and quality of bean.	Length of bean.	Vanillin.	Normal lead number.	Color value.				Per cent of total color in lead filtrate.		Ratio of red to yellow.		Per cent of total color in- soluble in amyl alcohol.
					Extract (total color).		Lead filtrate. ¹				Extract.	Lead filtrate.	
					Red.	Yellow.	Red.	Yellow.	Red.	Yellow.			
	Mexican:	cm.	Gms. per 100 cc.						Per cent.	Per cent.			Per cent.
1	First.....	22	0.17	0.52	22	62	1.2	4.8	5	8	1:2.8	1:4.0	19.5
2	Do.....	17	.16	.47	19	55	1.2	4.8	6	9	2.9	4.0	23.9
3	Second.....	22	.17	.56	25	80	1.4	7.0	6	9	3.2	5.0	21.3
4	Do.....	19	.17	.55	25	72	1.0	4.8	4	7	2.9	4.8	19.5
5	Do.....	15	.17	.61	29	75	1.2	5.4	4	7	2.6	4.5	20.5
6	Third.....	23	.19	.58	27	102	1.4	7.8	5	8	3.8	5.6	22.7
7	Do.....	19	.19	.59	27	97	1.4	6.2	5	6	3.6	4.4	24.4
8	Do.....	15	.20	.50	30	97	1.4	6.2	5	6	3.2	4.4	21.1
9	Third (splits).....	21	.19	.62	50	135	1.8	7.8	4	6	2.7	4.3	20.4
10	Fourth.....	20	.19	.64	35	102	1.4	6.8	4	7	2.9	4.9	20.4
11	Fifth.....	22	.15	.66	35	115	1.8	7.6	5	7	3.3	4.2	20.8
12	Do.....	16	.16	.68	37	120	1.8	7.8	5	7	3.2	4.3	22.2
13	Cuts.....		.16	.62	56	154	2.0	8.0	4	5	2.8	4.0	19.0
	Maximum.....	23	.20	.68	56	154	2.0	8.0	6	9	3.8	5.6	24.4
	Minimum.....	15	.15	.47	19	55	1.0	4.8	4	5	2.6	4.0	19.0
	Average.....	19	.17	.58	32	97	1.5	6.5	5	7	3.1	4.5	21.2
	Bourbon:												
14	First.....	22	.20	.46	22	65	1.8	6.4	8	10	3.0	3.6	27.0
15	Do.....	16	.20	.49	22	67	1.8	6.8	8	10	3.0	3.8	29.4
16	Do.....	13	.19	.49	22	67	1.6	6.2	7	9	3.0	3.9	27.8

¹ Calculated to volume of extract.

TABLE 1.—Analyses of vanilla extracts (tincture of vanilla U. S. P.) made in the laboratory—Continued.

Serial No.	Kind and quality of bean.	Length of bean.	Vanillin.	Normal lead number.	Color value.				Per cent of total color in lead filtrate.		Ratio of red to yellow.		Per cent of total color in- soluble in amyl alcohol.
					Extract (total color).		Lead filtrate.				Extract.	Lead filtrate.	
					Red.	Yellow.	Red.	Yellow.	Red.	Yellow.			
		cm.	Gms. per 100 cc.					Per cent.	Per cent.			Per cent.	
	Bourbon—Contd.	22	.15	.55	22	68	1.4	5.8	6	9	3.1	4.1	29.4
17	Second.....	17	.20	.62	55	127	2.4	6.8	4	5	2.3	2.8	24.4
18	Do.....	11	.21	.63	30	110	1.8	8.2	6	7	3.7	4.6	29.4
19	Do.....	22	.22	.52	25	80	2.0	7.0	8	9	3.2	3.5	27.8
20	Third.....	15	.20	.44	25	97	1.4	7.0	6	7	3.9	5.0	27.0
21	Do.....	10	.17	.55	30	104	2.0	7.6	7	7	3.5	3.8	26.3
22	Do.....	19	.19	.49	44	115	2.0	8.0	5	7	2.6	4.0	23.3
23	Third (splits).....	22	.15	.48	30	90	1.8	6.2	6	7	3.0	3.4	26.5
24	Fourth.....	15	.14	.50	25	98	1.8	6.8	7	7	3.9	3.8	20.3
25	Do.....	10	.13	.54	25	90	2.0	6.8	8	7	3.6	3.4	27.0
26	Do.....	22	.14	.52	32	107	2.0	7.8	6	7	3.3	3.9	21.3
27	Fifth.....	15	.15	.56	40	115	2.0	6.8	5	6	2.9	3.4	21.7
28	Do.....	10	.16	.55	32	97	1.8	7.6	6	8	3.0	4.2	26.3
29	Do.....												
	Maximum.....	22	.22	.63	55	127	2.4	8.2	8	10	3.9	5.0	30.3
	Minimum.....	10	.13	.44	22	65	1.4	5.8	4	5	2.3	2.8	21.3
	Average.....	16	.18	.52	30	94	1.9	7.0	6	8	3.2	3.8	26.6
	Seychelles:												
30	First.....	20	.19	.46	22	80	1.0	5.0	4	6	3.6	5.0	23.3
31	Do.....	15	.19	.41	23	77	1.2	5.8	5	8	3.3	4.8	22.7
32	Do.....	10	.20	.52	22	77	1.4	6.0	6	8	3.5	4.3	27.0
33	Third.....	22	.21	.45	25	87	1.4	6.6	6	8	3.5	4.7	25.1
34	Do.....	15	.19	.51	47	117	2.2	8.8	5	8	2.5	4.0	25.1
35	Do.....	11	.19	.54	39	115	1.8	8.2	5	7	2.9	4.6	27.0
36	Fourth.....	22	.21	.51	50	162	3.4	14.6	7	9	3.2	4.3	29.4
37	Do.....	15	.18	.60	38	120	2.0	8.2	5	7	3.1	4.1	25.0
38	Do.....	10	.16	.59	35	125	1.8	8.2	5	7	3.6	4.6	25.6
	Maximum.....	22	.21	.60	50	162	3.4	14.6	7	9	3.6	5.0	29.4
	Minimum.....	10	.16	.45	22	77	1.0	5.0	4	6	2.5	4.0	22.7
	Average.....	16	.19	.51	33	107	1.8	7.9	5	8	3.2	4.5	25.6
	Madagascar:												
39	Second.....	23	.23	.42	25	87	1.6	7.2	6	8	3.5	4.5	24.3
40	Do.....	17	.23	.40	25	85	1.4	6.2	6	7	3.4	4.4	25.0
41	Do.....	11	.19	.46	31	85	1.8	7.6	6	9	2.7	4.2	23.2
42	Third.....	22	.21	.55	30	102	2.4	8.4	7	8	3.4	3.5	27.8
43	Do.....	15	.21	.61	47	147	1.8	9.2	4	6	3.1	5.1	27.8
44	Do.....	12	.16	.63	42	120	1.8	9.2	4	8	2.9	5.1	28.6
45	Fourth.....	20	.30	.49	42	148	2.6	11.5	6	8	3.5	4.4	30.3
46	Do.....	15	.24	.41	30	110	1.8	9.0	6	8	3.3	5.0	27.8
47	Do.....	12	.24	.51	37	115	2.4	10.0	7	9	3.1	4.2	26.3
	Maximum.....	23	.30	.63	47	148	2.6	11.5	7	9	3.5	5.1	30.3
	Minimum.....	11	.16	.40	25	85	1.4	6.2	4	6	2.7	3.5	23.2
	Average.....	16	.22	.50	34	111	2.0	8.7	6	8	3.2	4.5	26.8
	Comores:												
48	First ¹	21	.19	.52	30	90	1.4	6.6	5	7	3.0	4.7	26.3
49	Do.....	15	.18	.54	30	107	1.8	6.4	6	6	3.6	3.6	28.6
50	Do.....	11	.18	.59	25	95	2.0	7.0	8	8	3.8	3.5	25.0
51	Third ¹	19	.19	.59	35	115	2.2	7.6	6	7	3.3	3.5	25.6
52	Do.....	15	.17	.59	30	107	1.8	7.4	6	7	3.6	4.1	25.0
53	Do.....	10	.15	.68	30	92	2.2	7.4	7	8	3.1	3.4	28.6
54	Fourth ¹	19	.12	.74	40	140	2.4	9.2	6	7	3.5	3.4	26.3
55	Do.....	14	.12	.71	32	105	2.4	8.4	7	8	3.3	3.5	27.0
56	Do.....	10	.15	.64	37	105	2.4	8.6	6	8	2.8	3.6	25.6
57	First ²	21	.31	.40	26	77	1.8	7.0	7	9	3.0	3.9	26.3
58	Do.....	15	.22	.52	27	87	1.4	7.4	5	8	3.2	5.3	28.6
59	Second ²	15	.25	.48	40	134	2.6	12.6	7	9	3.3	4.8	35.7
60	Fourth ²	15	.12	.73	37	107	2.0	9.6	7	9	2.9	4.8	30.3
61	First ³	15	.20	.48	22	70	1.4	6.0	6	8	3.2	4.3	24.4
62	Third ³	15	.20	.55	26	77	1.4	6.0	5	8	3.0	4.3	20.4
63	Fourth ³	15	.16	.65	27	77	1.4	6.2	5	8	2.9	4.4	23.7
	Maximum.....	21	.31	.74	40	140	2.6	12.6	8	9	3.8	5.3	30.3
	Minimum.....	10	.12	.40	22	70	1.4	6.0	5	6	2.8	3.4	20.4
	Average.....	15	.18	.59	31	99	1.9	7.7	6	8	3.2	4.1	26.7

¹ Pomoni, Anjouan.² Comoro.³ Mayotte.

TABLE 1.—Analyses of vanilla extracts (tincture of vanilla U. S. P.) made in the laboratory—Continued.

Serial No.	Kind and quality of bean.	Length of bean.	Vanillin.	Normal lead number.	Color value.				Per cent of total color in lead filtrate.		Ratio of red to yellow.		Per cent of total color in- soluble in amyl alcohol.
					Extract (total color).		Lead filtrate.				Extract.	Lead filtrate.	
					Red.	Yellow.	Red.	Yellow.	Red.	Yellow.			
		cm.	Gms. per 100 cc.					Per cent.	Per cent.			Per cent.	
64	South American:												
65	First.....	.23	.50	50	155	2.6	10.4	5	6	3.1	4.0	29.4	
66	Second.....	.19	.58	42	130	2.4	8.4	6	6	3.1	3.5	20.0	
	Splits.....	.22	.49	46	117	1.8	6.8	4	6	2.5	3.8	20.4	
	Maximum.....	.23	.58	50	155	2.6	10.4	6	6	3.1	4.0	29.4	
	Minimum.....	.19	.49	42	117	1.8	6.8	4	6	2.5	3.5	20.0	
	Average.....	.21	.52	46	134	2.3	8.5	5	6	2.9	3.8	23.3	
67	Ceylon:												
68	First.....	20	.08	.67	40	145	1.4	6.4	4	4	3.6	4.6	22.7
69	Do.....	17	.08	.62	42	147	3.8	15.6	9	11	3.5	4.1	35.7
	Do.....	12	.07	.57	61	195	7.6	32.6	12	17	3.2	4.3	50.0
	Maximum.....	20	.08	.67	61	195	7.6	32.6	12	17	3.6	4.6	50.0
	Minimum.....	12	.07	.57	40	145	1.4	6.4	4	4	3.2	4.1	22.7
	Average.....	16	.08	.62	48	162	4.3	18.2	8	11	3.4	4.3	36.1
70	Java:												
71	Fourth.....	20	.23	.61	45	177	2.4	10.4	5	6	3.9	4.3	32.2
72	Do.....	14	.24	.44	44	142	3.2	13.4	7	9	3.2	4.2	35.7
	Do.....	10	.22	.44	44	130	3.0	12.4	7	10	3.0	4.1	35.7
	Maximum.....	20	.24	.61	45	177	3.2	13.4	7	10	3.9	4.3	35.7
	Minimum.....	10	.22	.44	44	130	2.4	10.4	5	6	3.0	4.1	32.2
	Average.....	15	.23	.50	44	150	2.9	12.1	6	8	3.4	4.2	34.5
73	Tahiti:												
7411	.50	17	50	.6	3.5	4	7	3.0	5.8	18.8	
11	.44	15	40	.6	3.1	4	8	2.7	5.2	16.0	
	Average.....	.11	.47	16	45	.6	3.3	4	8	2.9	5.5	17.4	
75	Vanillons:												
06	.52	42	107	1.4	6.6	3	6	2.5	4.7	22.2	
76	Tonka beans:												
77	Angostura—												
	Prime.....	(1)	.11	5	18	.5	2.4	10	13	3.6	4.8	30.3	
	Bloaters.....	(2)	.11	5	19	.5	2.4	10	13	3.8	4.8	31.2	
	Average.....	(3)	.11	5	19	.5	2.4	10	13	3.7	4.8	30.8	
	All analyses: 4												
	Maximum.....	23	.31	.74	56	177	3.4	14.6	8	10	3.9	5.8	35.7
	Minimum.....	10	.11	.40	15	40	.6	3.1	4	5	2.3	2.8	16.0
	Average.....	16	.19	.54	32	102	1.8	7.6	6	8	3.2	4.2	25.5

1 Coumarin, 0.27 per cent.

2 Coumarin, 0.22 per cent.

3 Coumarin, 0.25 per cent.

4 Excluding Ceylon vanilla, Vanillons, and Tonka beans.

TABLE 2.—Analyses of extracts made from residues from vanilla extracts (Table 1) by soaking in 60 per cent alcohol.

[Results calculated to volume of U. S. P. extract.]

Serial number.	Kind and quality of bean.	Length of bean.	Vanillin.	Normal lead number.	Color value.				Per cent of total color in lead filtrate.		Ratio of red to yellow.	
					Extract (total color).		Lead filtrate.		Red.	Yellow.	Ex-tract.	Lead filtrate.
					Red.	Yellow.	Red.	Yellow.				
		cm.	Grams per 100 cc.						Per cent.	Per cent.		
1	Mexican:											
2	First.....	22	0.03	0.05	7	26	0.20	0.8	3	3	1:3.7	1:4.0
3	Do.....	17	.03	.05	9	28	.30	1.0	3	3	3.1	3.3
4	Second.....	22	.02	.11	16	50	.40	1.7	3	3	3.1	4.2
5	Do.....	19	.04	.09	11	41	.25	1.3	2	3	3.7	5.2
6	Do.....	15	.04	.06	10	32	.25	1.1	3	3	3.2	4.4
7	Third.....	23	.03	.05	8	28	.25	1.0	3	3	3.5	4.0
8	Do.....	19	.02	.05	4	21	.25	1.0	6	5	5.2	4.0
9	Do.....	15	.02	.06	5	23	.20	1.0	4	4	4.6	5.0
10	Third (splits).....	21	.03	.07	13	37	.35	1.3	3	4	2.8	3.7
11	Fourth.....	20	.03	.06	6	24	.25	1.0	4	4	4.0	4.0
12	Fifth.....	22	.03	.06	6	22	.20	1.0	3	5	3.7	5.0
13	Do.....	16	.03	.07	7	23	.30	1.0	4	4	3.3	3.3
14	Cuts.....		.02	.05	9	25	.25	1.1	3	4	2.8	4.4
15	Bourbon:											
16	First.....	22	.05	.05	10	30	.25	1.3	2	4	3.0	5.2
17	Do.....	16	.05	.05	9	26	.35	1.1	4	4	2.9	3.1
18	Do.....	13	.05	.06	8	24	.35	1.2	4	5	3.0	3.4
19	Second.....	22	.03	.05	13	40	.30	1.1	2	3	3.1	3.7
20	Do.....	17	.03	.05	13	33	.30	1.0	2	3	2.5	3.3
21	Do.....	11	.04	.05	10	31	.30	1.1	3	4	3.1	3.7
22	Third.....	22	.05	.07	13	37	.40	1.8	3	5	2.8	4.5
23	Do.....	15	.04	.04	9	31	.35	1.2	4	4	3.4	3.4
24	Do.....	10	.03	.04	8	27	.25	1.0	3	4	3.4	4.0
25	Third (splits).....	19	.04	.05	9	31	.20	1.2	2	4	3.4	6.0
26	Fourth.....	22	.04	.06	8	30	.25	1.3	3	4	3.7	5.2
27	Do.....	15	.03	.04	6	25	.25	1.1	4	5	4.2	4.4
28	Do.....	10	.03	.05	6	24	.25	1.0	4	4	4.0	4.0
29	Fifth.....	22	.04	.08	13	47	.30	1.8	2	4	3.6	6.0
30	Do.....	15	.04	.08	14	38	.30	1.5	2	4	2.7	5.0
31	Do.....	10	.03	.03	11	30	.25	1.3	2	4	2.7	5.2
32	Seychelles:											
33	First.....	20	.04	.04	8	30	.20	1.0	3	3	3.7	5.0
34	Do.....	15	.04	.04	8	36	.20	1.1	3	3	4.5	5.5
35	Do.....	10	.03	.04	8	26	.15	.8	2	3	3.2	5.3
36	Third.....	22	.04	.04	8	28	.20	1.0	3	4	3.5	5.0
37	Do.....	15	.04	.06	8	30	.20	1.3	3	4	3.7	6.5
38	Do.....	11										
39	Fourth.....	22	.04	.05	11	34	.50	1.5	5	4	3.1	3.0
40	Do.....	15	.04	.06	16	51	.40	1.7	3	3	3.2	4.2
41	Do.....	10	.03	.04	9	30	.20	1.1	2	4	3.3	5.5
42	Madagascar:											
43	Second.....	23	.05	.04	13	48	.30	1.1	2	2	3.7	3.7
44	Do.....	17	.05	.05	14	49	.30	1.1	2	2	3.5	3.7
45	Do.....	11	.03	.05	9	30	.25	1.0	3	3	3.3	4.0
46	Third.....	22	.06	.06	13	47	.35	1.3	3	3	3.6	3.7
47	Do.....	15	.03	.05	9	26	.25	1.3	3	5	2.9	5.2
48	Do.....	12	.04	.08	11	36	.35	1.3	3	4	3.3	3.7
49	Fourth.....	20	.04	.04	10	26	.30	1.4	3	5	2.6	4.7
50	Do.....	15	.04	.06	9	30	.30	1.3	3	4	3.3	4.3
51	Do.....	12	.03	.05	13	34	.40	1.7	3	5	2.6	4.2
52	Comores:											
53	First ¹	21	.03	.04	8	27	.25	1.1	3	4	3.4	4.4
54	Do.....	15	.02	.04	8	28	.20	1.1	2	4	3.5	5.5
55	Do.....	11	.02	.04	8	25	.25	.8	3	3	3.1	3.2
56	Third ¹	19	.03	.04	8	26	.20	1.3	3	5	3.2	6.5
57	Do.....	15	.03	.05	7	25	.20	1.1	3	4	3.6	5.5
58	Do.....	10	.01	.04	6	21	.20	1.0	3	5	3.5	5.0
59	Fourth ¹	19	.04	.07	10	36	.35	1.6	4	4	3.6	4.6
60	Do.....	14	.03	.06	9	34	.30	1.5	3	4	3.8	5.0
	Do.....	10	.03	.05	8	30	.25	1.3	3	4	3.7	5.2
	First ²	21	.04	.04	11	42	.20	1.3	2	3	3.8	6.5
	Do.....	15	.02	.03	7	24	.20	1.0	3	4	3.4	5.0
	Second ²	15	.07	.06	17	62	.35	2.2	2	4	3.6	6.3
	Fourth ²	15	.03	.05	7	27	.30	1.1	4	4	3.9	3.7

¹ Pomoni, Anjouan.² Comoro.

TABLE 2.—Analyses of extracts made from residues from vanilla extracts (Table 1) by soaking in 60 per cent alcohol—Continued.

Serial number.	Kind and quality of bean.	Length of bean.	Vanillin.	Normal lead number.	Color value.				Per cent of total color in lead filtrate.		Ratio of red to yellow.	
					Extract (total color).		Lead filtrate.		Red.	Yellow.	Ex-tract.	Lead filtrate.
					Red.	Yellow.	Red.	Yellow.				
	Comores— Contd.	cm.	Grams per 100 cc.						Per cent.	Per cent.		
61	First 1.....	15	.04	.07	13	41	.25	1.6	2	4	3.2	6.4
62	Third 1.....	15	.04	.09	15	46	.25	1.6	2	3	3.1	6.4
63	Fourth 1.....	15	.03	.07	10	33	.20	1.3	2	4	3.3	6.5
	South American:											
64	First.....		.04	.04	11	40	.30	1.5	3	4	3.6	5.0
65	Second.....		.04	.07	13	48	.25	1.6	2	3	3.7	6.4
66	Splits.....		.04	.05	11	40	.25	1.2	2	3	3.6	4.8
	Ceylon:											
67	First.....	20	.03	.07	6	24	.20	1.1	3	5	4.0	5.5
68	Do.....	17	.02	.06	8	30	.30	1.7	4	6	3.7	5.7
69	Do.....	12	.01	.04	6	25	.25	1.6	4	6	4.2	6.4
	Java:											
70	Fourth.....	20	.05	.04	7	29	.45	1.6	6	6	4.1	3.6
71	Do.....	14	.04	.04	7	28	.25	1.4	4	5	4.0	5.6
72	Do.....	10	.03	.04	4	23	.28	1.3	7	6	5.7	4.6
73	Tahiti:		.02	.05	7	23	.25	.9	4	4	3.3	3.6
7401	.05	8	29	.20	.8	3	3	3.6	4.0
	Vanillons:											
7501	.06	15	46	.25	1.2	2	3	3.1	4.8
	Tonka beans:											
76	Angostura prime.....		.00	.04	1	6	.10	.5	10	8	6.0	5.0
77	Angostura bloaters.....		.00	.04	1	6	.10	.4	10	7	6.0	4.0
	All analyses:											
	Maximum.....		.07	.11	17	62	.50	2.2	7	6	5.7	6.5
	Minimum.....		.01	.03	4	21	.15	.8	2	2	2.5	3.0
	Average.....		.03	.05	9	32	.27	1.2	3	4	3.4	4.6

¹ Mayotte.

DISCUSSION OF RESULTS.

The extracts from the three lengths of Ceylon beans were so abnormal and variable in composition as to indicate that either the beans had been cured by an unusual process or else exhausted and treated in some manner to disguise the fact. The vanillin in all of the samples was abnormally low, while the percentage of color left in the lead filtrate, while abnormally low in the extract from the long beans, was abnormally high in that from the short beans. This bean is uncommon in our market.

Vanillin.—The range in vanillin content (0.11–0.31 gram per 100 cc) is somewhat greater than has usually been thought possible. Leach states that an extract containing as high as 0.25 per cent of vanillin is suspicious, which is doubtless true of extracts made on a large scale, just as abnormal percentages of fat which may occur in the milk of individual cows will not be found in the milk of a mixed herd. The extract from the residue corresponding to the sample containing the maximum percentage of vanillin (0.31) gave 0.04 additional, making the total 0.35.

The minimum figure (0.11) was found in the Tahiti extracts, which were prepared from undried beans. Had dried beans been used, as is the custom in

the trade, the percentages of all the constituents would have been materially higher.

Normal lead number.—The variation in lead number (from 0.40–0.74) is less than that of any other of the constants. The constituents which give the precipitate appear to be more easily soluble than the vanillin and color, the second extraction yielding an average normal lead number of only 0.05. This determination not only serves to distinguish a true extract from a solution of vanillin, but also is of value in conjunction with the determination of coumarin as a means of detecting the presence of Tonka extract.

Color values of extract and lead filtrate.—The color appears to be the most variable and most difficultly extractable constituent. As a means of detecting caramel, the per cent of color left in the lead filtrate is most significant. The maximum found in these samples (excluding Ceylon) was 8 per cent red and 10 per cent yellow, whereas one of the samples colored with caramel sent out during the year 1911 by Mr. Hiltner, as associate referee on extracts, gave, respectively, 20 per cent and 37 per cent, and commercial extracts have given similar figures. The ratio of red to yellow in the extract and lead filtrate is also of value, as caramel solution shows a lower ratio, or, in other words, is redder. The minimum ratio found in our extracts was 1:2.3, as compared with 1:1.9 in Mr. Hiltner's sample.

Per cent of color insoluble in amyl alcohol.—The results corroborate those obtained in the determination of the per cent of color in the lead filtrate, with the advantage that they are not so cumbersome and do not require a tintometer. On the other hand, this determination requires an additional process, whereas the color values of the lead filtrate are obtained incidentally in the determination of vanillin and lead number.

Influence of grade of bean on the constants of the extract.—In the following table are given the average figures for extracts from the five grades of all the varieties of vanilla beans, excluding South America, Java, and Tahiti, of which there were only one or two grades, and Ceylon, which was abnormal:

TABLE 3.—Averages of analyses of U. S. P. vanilla extracts according to grade of bean.

Grade of bean.	Number of samples.	Vanillin.	Normal lead number.	Color value.				Per cent of total color in lead filtrate.		Ratio of red to yellow.		Per cent of total color insoluble in amyl alcohol.
				Extract (total color).		Lead filtrate.				Ex-tract.	Lead fil-trate.	
				Red.	Yel-low.	Red.	Yel-low.	Red.	Yel-low.			
		<i>Grams per 100 cc.</i>						<i>Per cent.</i>	<i>Per cent.</i>			<i>Per cent.</i>
First.....	14	0.20	0.49	24	77	1.5	6.1	6	8	1 : 3.2	1 : 4.2	25.7
Second.....	10	.20	.53	31	92	1.7	7.2	6	8	3.1	4.4	25.3
Third.....	16	.19	.55	32	104	1.8	7.6	6	7	3.3	4.3	25.7
Fourth.....	15	.17	.58	35	113	2.1	8.7	6	8	3.2	4.1	26.8
Fifth.....	5	.15	.59	35	111	1.9	7.5	5	7	3.1	4.0	22.5

These figures show, from the lowest to the highest grade, a marked increase of vanillin and a marked decrease of normal lead number and color value. In this connection it should be noted that the Tahiti extracts, the cheapest of all, while containing the lowest amounts of vanillin, are exceptional in that the color values are also lowest, while the normal lead numbers are inter-

mediate. It must, therefore, be understood that the conclusions reached are relative, applying only to the different grades of the same or related varieties.

Influence of length of bean on the constants of the extract.—The average results of analyses of extracts from long, medium, and short beans, excluding South American and Tahiti, which were not sorted by lengths, and Ceylon, which were abnormal, are shown in the following table:

TABLE 4.—Averages of analyses of U. S. P. vanilla extracts according to length of bean.

Length of bean.	Number of samples.	Vanillin.	Normal lead number.	Color value.				Per cent of total color in lead filtrate.		Ratio of red to yellow.		Per cent of total color insoluble in amyl alcohol.
				Extract (total color).		Lead filtrate.				Ex-tract.	Lead fil-trate.	
				Red.	Yel-low.	Red.	Yel-low.	Red.	Yel-low.			
cm.		Grams per 100 cc.						Per cent.	Per cent.			Per cent.
20-23	19	0.20	0.52	30	99	1.8	7.6	6	8	1 : 3.3	1 : 4.3	25.3
15-19	27	.18	.55	32	100	1.7	7.2	6	7	3.2	4.3	25.4
10-14	17	.18	.56	33	104	2.1	8.4	6	8	3.2	4.1	27.8

A slight increase in vanillin and decrease in normal lead number and color values from the shortest to the longest beans is noticeable. These differences, although not marked, point to a slight inferiority of the shorter beans.

VANILLA EXTRACTS PREPARED WITH DIFFERENT MENSTRUUA IN THE LABORATORY.

PREPARATION OF EXTRACTS.

Six extracts were made from each of three typical varieties of beans, viz. Mexican, Bourbon, and Tahiti, using the following menstrua: (1) Sixty per cent alcohol only; (2) 60 per cent alcohol and sugar (U. S. P.); (3) 60 per cent alcohol and glycerin; (4) 35 per cent alcohol only; (5) 35 per cent alcohol and sugar; (6) 35 per cent alcohol and glycerin. In all cases two liters of extract were made from 200 grams of the ground material.

The extracts made with 60 per cent alcohol and sugar were the usual U. S. P. preparations, as were also those made with 35 per cent alcohol and sugar, except as regards the strength of the alcohol.

In preparing the glycerin extracts 200 cc of glycerin were first mixed with the ground beans, after which the manipulation was the same as in the U. S. P. process, except that the material, after maceration and draining off the liquid, was pounded in a mortar with 200 grams of sand instead of sugar. One set of these glycerin extracts was made with 60 per cent alcohol, the other with 35 per cent alcohol.

The alcohol extracts were made with 60 per cent and 35 per cent alcohol, without the addition of either sugar or glycerin, the manipulation in these also being the same as in the U. S. P. process, except for the substitution of 200 grams of sand for sugar.

The preparation of the extracts with 35 per cent alcohol, both with and without sugar or glycerin, was highly unsatisfactory, owing to the extraction of gelatinous material, which clogged the percolators. It was found necessary to

loosen up the material repeatedly, and as a consequence the percolate was a muddy liquid containing seeds and other matters in suspension. These mechanical impurities were partially removed by long settling and filtration of the supernatant liquid. This process could not be carried out to advantage on a commercial scale, and consequently the extracts do not represent products on the market, but rather abnormal preparations useful in illustrating the effects of diluting the alcohol beyond a certain limit.

In all cases second extracts were prepared from the residues from the first extracts by soaking in 60 per cent alcohol, as already described.

ANALYSES OF THE EXTRACTS.

The analyses of the first extracts appear in Table 5, and of the extracts made from the residues in Table 6.

TABLE 5.—*Analyses of vanilla extracts prepared with different menstrua in the laboratory.*

Kind of bean and menstruum.	Vanil- lin.	Lead num- ber.	Color value.				Per cent of total color in lead filtrate.		Ratio of red to yellow.		Total color insoluble in amyl alcohol
			Extract (total color).		Lead fil- trate. ¹				Ex- tract.	Lead fil- trate.	
			Red.	Yel- low.	Red.	Yel- low.	Red.	Yel- low.			
	<i>Gms. per 100 cc.</i>						<i>Per cent.</i>	<i>Per cent.</i>			<i>Per cent.</i>
Mexican:	0.19	0.70	33	103	1.8	7.1	5.5	6.9	1:3.1	1:3.9	18.6
60 per cent alcohol.....	.19	.65	35	103	2.0	8.6	5.7	8.4	2.9	4.3	24.4
60 per cent alcohol and sugar (U. S. P.).....	.16	.69	41	123	2.0	8.8	4.9	7.2	3.0	4.4	22.7
60 per cent alcohol and glycerin.....	.17	.82	31	75	1.8	6.6	5.8	8.8	2.4	3.7	27.8
35 per cent alcohol.....	.17	.79	28	75	2.0	7.5	7.1	10.0	2.4	3.8	38.5
35 per cent alcohol and sugar.....	.18	.80	40	90	2.0	7.5	5.0	8.3	2.3	3.8	35.7
35 per cent alcohol and glycerin.....											
Bourbon:											
60 per cent alcohol.....	.19	.61	34	108	1.9	8.2	5.6	7.6	3.2	4.3	20.5
60 per cent alcohol and sugar (U. S. P.).....	.19	.57	39	119	2.4	10.0	6.2	8.4	3.1	4.2	25.1
60 per cent alcohol and glycerin.....	.20	.58	43	133	2.0	9.6	4.7	7.2	3.1	4.8	25.0
35 per cent alcohol.....	.17	.71	30	73	1.8	7.0	6.0	9.6	2.4	3.9	34.5
35 per cent alcohol and sugar.....	.17	.66	31	78	2.2	8.0	7.1	10.3	2.4	3.6	45.4
35 per cent alcohol and glycerin.....	.19	.68	50	110	2.4	8.4	4.8	7.6	2.2	3.5	38.5
Tahiti:											
60 per cent alcohol.....	.11	.43	13	40	.6	2.6	4.6	6.5	3.1	4.3	14.3
60 per cent alcohol and sugar (U. S. P.).....	.11	.44	15	40	.6	3.1	4.0	7.7	2.7	5.2	16.0
60 per cent alcohol and glycerin.....	.11	.43	24	53	.7	3.3	2.9	6.2	2.2	4.7	15.9
35 per cent alcohol.....	.09	.39	15	30	1.2	4.0	8.0	13.3	2.3	3.3	23.8
35 per cent alcohol and sugar.....	.09	.44	15	33	1.3	4.4	8.7	13.9	2.2	3.4	28.6
35 per cent alcohol and glycerin.....	.10	.40	15	33	.9	3.3	6.0	10.0	2.0	3.6	24.4

¹ Calculated to volume of extract.

TABLE 6.—*Analyses of extracts prepared from residues from vanilla extracts (Table 5) by soaking in 60 per cent alcohol.*

[Results calculated to volume of U. S. P. extract.]

Kind of bean and menstruum.	Vanillin.	Normal lead number.	Color value.				Per cent of total color in lead filtrate.		Ratio of red to yellow.	
			Extract (total color).		Lead filtrate.					
			Red.	Yellow.	Red.	Yellow.	Red.	Yellow.	Extract.	Lead filtrate.
	<i>Grams per 100 cc.</i>									
Mexican:										
60 per cent alcohol.....	0.04	0.07	11	31	0.3	1.1	2.7	3.5	1:2.8	1:3.7
60 per cent alcohol and sugar.....	.04	.09	13	38	.3	1.2	2.3	3.2	2.9	4.0
60 per cent alcohol and glycerin.....	.04	.06	6	25	.3	1.05	5.0	4.2	4.2	3.5
35 per cent alcohol.....	.03	.05								
35 per cent alcohol and sugar.....	.03	.05								
35 per cent alcohol and glycerin.....	.03	.04								
Bourbon:										
60 per cent alcohol.....	.04	.06	11	31	.3	1.2	2.7	3.9	2.8	4.0
60 per cent alcohol and sugar.....	.04	.06	11	30	.35	1.2	3.2	4.0	2.7	3.4
60 per cent alcohol and glycerin.....	.04	.04	8	24	.35	1.25	4.4	5.2	3.0	3.6
35 per cent alcohol.....	.03	.05								
35 per cent alcohol and sugar.....	.05	.06								
35 per cent alcohol and glycerin.....	.04	.04								
Tahiti:										
60 per cent alcohol.....	.01	.03	6	19	.2	.8	3.3	4.2	3.2	4.0
60 per cent alcohol and sugar.....	.01	.05	8	29	.2	.8	2.5	2.8	3.6	4.0
60 per cent alcohol and glycerin.....	.01	.05	4	13	.2	.85	5.0	6.5	3.2	4.2
35 per cent alcohol.....	.01	.03								
35 per cent alcohol and sugar.....	.01	.03								
35 per cent alcohol and glycerin.....	.01	.03								

INFLUENCE OF GLYCERIN AND SUGAR AND STRENGTH OF ALCOHOL ON COMPOSITION.

When the same strength of alcohol was employed the only noteworthy difference brought out by analysis was that the glycerin extracts were more strongly colored than when alcohol alone or alcohol and sugar were used. This explains in part why glycerin is so much used in the manufacture of commercial extracts. The percentages of vanillin and normal lead number are practically the same whether or not glycerin or sugar was used. The color values of the second extracts made from the residues from the glycerin extracts were lower than those of the others, corresponding to the excess of color in the first extracts.

The difference in the extractive power of 60 per cent and 35 per cent alcohol, while not noticeable as regards vanillin, is marked as regards the other constituents. The weaker alcohol gave higher normal lead numbers, lower color values of the extract and higher percentages of color remaining both in the lead filtrate and insoluble in amyl alcohol.

STANDARD VANILLA EXTRACT.

The following tentative limits of composition for standard vanilla extract (10 grams of beans to 100 cc) appear to be warranted by the results obtained:

Vanillin, 0.10 to 0.35 gram per 100 cc.

Normal lead number, 0.40 to 0.80.

Per cent of total color in lead filtrate, not more than 10 per cent red or 12 per cent yellow.

Ratio of red to yellow in the extract, not less than 1:2.2.

Color insoluble in amyl alcohol, not more than 40 per cent.

REPORT ON COCOA AND COCOA PRODUCTS.

By W. L. DUBOIS, *Associate Referee.*

The work on cocoa products this year was confined to further testing of the short method for the determination of ether extract which was presented at the 1910 meeting of the association, and to the determination of milk solids in milk chocolate.

ETHER EXTRACT BY THE PROPOSED SHORT METHOD.

A sample of cocoa was sent to the collaborators with the following memorandum:

INSTRUCTIONS FOR COOPERATIVE WORK.

The method for the rapid determination of fat in cocoa products was presented to the association at its 1910 meeting (see Bul. 137, p. 103, for statement of method).

Two objections were brought against this method by the collaborators. One was that the filtering offered opportunity for the evaporation of the solvent and tended to give high results. It was contended that if the product were centrifuged long enough and care exercised in pouring the solvent from the cocoa material packed in the bottle, no necessity for the use of filtering paper would arise, it being sufficient to merely pour the ether through a small funnel into the burette. The experience of the referee differed on this point, some samples of cocoa seeming to pack well and others appearing to have so much fine material that it was almost impossible to pour off the ether without contaminating the same with some cocoa, which, of course, would tend to high results. It is therefore desired that the collaborators this year test this point and report their opinion as to whether filtering is necessary or desirable.

The second point is regarding the effect of hot weather upon the determination, two laboratories reporting that on very hot days there was an apparent evaporation of ether. The referee has not observed that higher results were obtained on warm days than on cool days, but such may be the case in laboratories where the temperature becomes quite high. It is therefore desired that the collaborators test this point also, determining the fat in the sample submitted under as ideal conditions as regards temperature as possible, and also on several very warm days, noting the temperature of the laboratory each time and reporting results obtained, together with a statement of opinion as to the point under consideration.

ANALYTICAL RESULTS.

A table is presented herewith to show results obtained by the different workers on this sample:

Cooperative results on ether extract by the short method testing effect of temperature and necessity of filtration.

Analyst.	Filtered.	Not filtered.	By continuous extraction.		Temperature.	Remarks.
			Petroleum ether.	Ether.		
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>° C.</i>	
C. I. Lott.....	23.09	22.80				
M. C. Albrech.....		23.01			29	
L. C. Mitchell.....	23.13	22.81		23.35		
	23.05	22.58		23.26		
N. Hendrickson.....	23.56				27	
	23.53					

Cooperative results on ether extract by the short method testing effect of temperature and necessity of filtration—Continued.

Analyst.	Filtered.	Not filtered.	By continuous extraction.		Temperature.	Remarks.
			Petroleum ether.	Ether.		
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>° C.</i>	
H. S. Bailey.....	24.45				29.5	
	23.43				29.5	
	23.43				22	
	23.86				24	
	23.06				24	
	25.07				29	
	24.63				29	
	23.85				20	
	23.20					
	23.41	22.97			25	
R. S. Hiltner.....		23.06			28	
				22.98	28	Knorr apparatus; sample not reextracted, fat not perfectly clear.
				22.87		Johnson extractor 4 hours, fat not perfectly clear.
				22.64		Leach-Hiltner method.
		22.64			18.5	
W. L. Dubois.....	24.49					
	24.39				29	
				23.37		Alundum thimble in Knorr apparatus.
			22.35			Do.

COMMENTS BY THE COLLABORATORS.

C. I. Lott: It seems to me important to stipulate that the ether used in this determination shall be at room temperature. If measured from a supply kept in the refrigerator, by the time the ether assumes the temperature of the room it will have expanded considerably so as to introduce a possible error from this source.

L. C. Mitchell: I see no use in filtering, as the sample was packed firmly.

M. C. Albrech: I have never found it necessary to filter, as I could always get the samples securely packed in the bottom of the bottle, so that the fat was entirely clear or was only slightly contaminated with cocoa material. In a large number of determinations I have frequently had one sample slightly contaminated with cocoa material and its duplicate entirely free, and there would be practically no difference in the duplicate results. I am strongly opposed to filtering the ether solution, as I think there is chance for error and evaporation, which errors are eliminated by avoiding filtration.

H. S. Bailey: I find that in ordinary summer temperature (85° to 90° F.) it is impossible to draw 50 cc of ether from a burette into an oil bottle and return the same to the burette without losing from 0.5 to 0.75 cc of the solvent, and when instead of an empty funnel a 7 cm filter paper was added the loss was three or four times as great. It appears to me, therefore, that it is impossible to filter the ether without introducing a very appreciable error in the determination. I think the fundamental ideas in the method are all right, and I see no reason why it should not be adopted for rapid work, if instead of filtering from the bottle into the burette this transfer be made as quickly as possible, and then, after noting the quantity of ether returned to the burette, the solvent with its fat will all be filtered into the tared flask.

R. S. Hiltner: It is evident that this method may be relied upon if the ether solution is poured directly into the burette and not filtered, and if the operation is conducted at a temperature not exceeding 25° C. and away from strong drafts. If the extracts are filtered the results will be erroneously high. Personally, I should prefer using a Johnson and Knorr extractor and extracting

the sample for four hours or longer, because less personal attention is required and because the method is less sensitive to atmospheric and temperature conditions.

DISCUSSION.

From the results obtained by the collaborators it is apparent that filtering of the fat solution is inadvisable, and that when this feature is omitted sufficiently accurate results can be obtained to make the proposition applicable to cocoa when a determination is desired in a short period of time. The manipulation is doubtless equal to that involved in the continuous extraction method, but the advantage of being able to obtain a result in shorter time remains.

While this method seems to be satisfactory for cocoa, some results have been obtained in this laboratory during the past year which throw some doubt upon its applicability to milk chocolates. By referring to the table of analyses of milk chocolates given on page 163 it will be seen that the results on ether extract are considerably lower by the proposed method than those obtained by continuous extraction with ether in Soxhlet's apparatus for 18 hours. This is probably due to the inability of ether to dissolve all of the butter fat, which is doubtless surrounded, at least in part, by an envelope of proteid material. An experiment on milk powder alone by this method gave results which were extremely low. While quite a number of figures have been reported in the past to support this short method as a reliable procedure for the determination of fat in milk chocolate, it seems that it may not always be above criticism when applied to this class of products. Some milk chocolates will doubtless yield their total fat more easily than others, depending upon the method of manufacture. Those chocolates which are made by mixing liquid milk with chocolate liquor and evaporating the whole together will doubtless present the butter fat in a more finely divided condition and therefore more easily extracted by the simple shaking with ether.

In view of the several uncertainties and sources of error, it seems to the referee that the method in question can be recommended as only an approximate one, to be used in cases where a quick determination is desired. It would not be his opinion, therefore, that the method should be recommended to the association for provisional adoption at this time.

SUBSTITUTION OF PETROLEUM ETHER FOR SULPHURIC ETHER.

Regarding the matter of fat determination in general in cocoa products, it has seemed to the referee for some time that the substitution of petroleum ether for sulphuric ether would be advisable. A small amount of the extract obtained by sulphuric ether seems to be other than cocoa fat. In a number of samples of cocoa which were extracted in the referee's laboratory by both petroleum ether and sulphuric ether, a slightly higher result was obtained by the latter. The extracted material, however, did not completely redissolve in ether, a white residue being apparent which was soluble in hot alcohol. It was thought that this might be theobromin, which is somewhat soluble in sulphuric ether, but the quantity obtainable was so small that attempts to crystallize the substance were unsuccessful. Theobromin is insoluble in petroleum ether, and the extracts obtained with petroleum ether on the above samples were completely soluble in ether, containing none of this white material, the extract being apparently all cocoa butter. Since cocoa butter is perfectly soluble in petroleum ether, there would seem to be no objection to the substitu-

tion referred to, while it appears that more accurate results are obtained thereby. Results on five cocoas follow:

Comparison of ether extract results using sulphuric and petroleum ether.

Sulphuric ether.	Petroleum ether.
<i>Per cent.</i>	<i>Per cent.</i>
23.07	22.74
29.39	28.86
28.12	27.52
24.99	24.40
23.15	22.56

With petroleum ether no more fat was obtained by extracting the collaborative sample for twelve hours and then grinding and extracting an additional four hours, than by simply extracting four hours without regrinding. While this was the case with this particular cocoa sample, however, it might not follow that such a short process would completely remove the fat from such products as chocolate and milk chocolate, in which cases the regrinding would probably be necessary. The wisdom of substituting petroleum ether for sulphuric ether, however, would hold with such products as well as with cocoa. The referee would recommend that this substitution be made.

MILK SOLIDS IN MILK CHOCOLATE.

Attempt was made to estimate the milk solids in milk chocolate by determining lactose, butter fat, and casein. Lactose was determined by the method reported last year (Bul. 137, p. 101) and recommended for provisional adoption; butter fat was estimated by determining the Reichert-Meissl number on ether extract and assuming 24 as the number of butter in making the calculation. It is necessary to make some deduction for the Reichert-Meissl number of cocoa butter, which, although small, is still appreciable. This number was determined on several cocoa butters obtained from manufacturers of cocoa products, and the results are given in the table. It was first thought that possibly the Koettstorfer number would assist in estimating butter fat, but it was found that the small amount of butter fat present would not introduce sufficient variation in this number to make it of value in the calculation. The results obtained on commercial cocoa butters, however, are included in the table:

Results on commercial cocoa butters.

No. of sample.	Reichert- Meissl number.	Koett- storfer number.
1	0.30	195.2
2	.20	193.3
3	.29	192.8
4	.60	193.6
5	.20	194.4
6	.10	192.4
7	.22	193.5
8	.10	194.8
9	.12	193.8
10	.60	193.0
11	.61	193.5

The average of these 11 Reichert-Meissl numbers is 0.30, but for the calculations on chocolate samples the value 0.50 was taken as probably representing a good average of commercial cocoa butter.

Casein was determined by extracting the fat from 3 grams of sample by shaking with ether, centrifuging, and drawing off the solvent. The residue was then treated three times with 30 cc of 1 per cent solution of sodium phosphate (Na_2PO_4), the bottle being heated to 60°C . each time for half an hour and shaken from time to time during this interval. It was then centrifuged and the supernatant liquid poured into a 200 cc flask. After the three extractions the volume was made up to 200 cc and 50 cc removed to a beaker to which 50 cc of water and 1 cc of 50 per cent solution of trichloroacetic acid were added, the solution brought to 100°C ., and the precipitate received on a tared filter, washed with hot water, dried, and weighed, and the casein computed from the increase in weight. This is doubtless a crude method for making this determination, since it was impossible to obtain a precipitate entirely free from cocoa tissue. The results proved approximate, however.

A sample of milk chocolate was prepared in the laboratory after the following formula :

	Per cent.
Chocolate.....	28
Sucrose.....	36
Milk powder.....	24
Cocoa butter.....	12

Besides this sample, three lots of milk chocolate were obtained from as many manufacturers, who stated the percentage of milk solids therein. Analyses of laboratory and commercial samples appear in the table :

Analyses of commercial and laboratory samples of milk chocolate.

Kind of chocolate.	Milk solids.	Lactose.	Fat.		Reichert-Meissl number (fat).	Koettstorfer number (fat).	Butter fat.	Casein.	Milk solids.
			Sohx.	Short.					
	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>			<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>
Laboratory.....	24	10.6	33.66	30.16	5.5	200	7.0	8.8	26.4
Huyler's.....	10	3.4	33.02	30.7	2.9	196.4	3.3	2.39	9.1
Peter's.....	17.4	6.07	33.25	31.0	4.5	199.3	5.5	7.1	18.66
Penna.....	17.6	6.20	32.42	30.5	4.0	200	4.7	7.2	18.1

It would seem from these results that the milk solids calculated from the determinations made are too high in every case but one. This may be due to contamination of the casein, as pointed out before, but there was not time for the referee to carry this investigation further.

REPORT ON TEA AND COFFEE.

By M. E. JAFFA, *Associate Referee.*

In accordance with the recommendations of last year the cooperative work during the current year on methods of analysis of tea and coffee has been confined mainly to the determinations of thein and caffeine. The following chemists collaborated in the work: J. A. Cummings and F. C. Woodruff, New York, N. Y.; A. L. Knisely, Portland, Oreg.; and G. R. Stewart and A. R. Mehrtens, Berkeley, Cal.

The methods employed in making these investigations are as follows:

METHODS OF ANALYSES.

TEA.

Determination of insoluble leaf and extract.—Method of Doolittle and Woodruff, Proceedings of 1906, Bulletin 105, page 48.

Determination of thein.—

(1) Dvorkovitch method, Bulletin 107, Revised, page 150; (2) Doolittle and Woodruff method, Proceedings of 1906, Bulletin 105, page 50; (3) Modification of Stahlschmidt's method: Boil 6 grams of finely powdered tea in a flask with several successive portions of water for 10 minutes each, and make up the combined aqueous extracts thus obtained to 600 cc with water. Add 4 grams of powdered lead acetate to the decoction, then boil for 10 minutes, using a reflux condenser or making up the loss by occasional addition of water. Then pour the solution upon a dry filter and evaporate 500 cc of the filtrate, corresponding to 5 grams of the tea, to about 50 cc and add enough sodium phosphate to precipitate the remaining lead. Filter the solution, and thoroughly wash the precipitate, the filtrate and washings being evaporated to about 40 cc. Finally, extract the solution thus concentrated with chloroform in a separatory funnel at least four times and evaporate the chloroform extract to dryness, leaving the caffeine, which is dried to constant weight at 75° and weighed.

Determination of caffeine.—

(1) The Gorter method (Proceedings in 1910, Bul. 137, p. 106); (2) method of Lendrich and Nottbohm (Zts. Nahr. Genussm., 1909, 17, 241; Proceedings of 1910, Bul. 137, p. 107). The following additional details were given in the direction for this year's work for the final steps of the method: "Evaporate the filtrate and washings to about 50 cc, make alkaline with sodium hydroxid, and extract four times with 25 cc, 20, 15, and 15 cc of chloroform. Evaporate in tared dish, dry for 30 minutes at 100 C. and weigh as caffeine. Transfer the caffeine to a Kjeldahl flask with a small amount of hot water and determine nitrogen in the residue as a check on its purity. ($N \times 3.464$ equals caffeine.)"

ANALYTICAL RESULTS.

Cooperative work on caffeine in coffee.

Collaborators.	Sample.	Gorter method.		Lendrich and Nottbohm method.	
		Gravimetric.	$N \times 3.464$.	Gravimetric.	$N \times 3.464$.
J. A. Cummings, New York, N. Y.	1. Decaffeinated.....	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
		0.43	0.13	0.09
		.40	0.15	.15
	2. Costa Rica.....	.35
		1.59	1.25	.56	.57
		1.57	1.23	.77	.76
	3. Java.....	1.78	1.26
		1.5096	.94
		1.42	1.16	1.05	1.03
	4. Mocha.....	1.44	1.18
		1.48	1.12	.84	.80
		1.52	1.22	1.10	1.10
G. R. Stewart and A. R. Mehrstens, Berkeley, Cal.	1. Decaffeinated.....	1.49	1.19
		.67	.15	.11	.09
		.48	.15	.12	.08
	2. Costa Rica.....	1.57	1.22	.62	.57
		1.64	1.26	.71	.65
		1.37	1.13	.78	.74
	3. Java.....	1.35	1.12	.62	.59
		1.40	1.09	.54	.51
		1.46	1.15	.55	.53
	4. Mocha.....	1.12
		1.50	1.24	.86	.80
		1.57	1.29	.80	.80
	5. Salvador.....
	
	

Cooperative work on tea.

Collaborators.	Sample.	Doolittle and Woodruff method.			Dvorkovitch method.		Modified Stahlschmidt method.	
		Insoluble leaf.	Caffein.		Caffein.		Caffein.	
			Gravimetric.	N× 3.464.	Gravimetric.	N× 3.464.	Gravimetric.	N× 3.464.
F. O. Woodruff, New York, N. Y.	6. English Break-fast.	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>	<i>Per ct.</i>
		44.9	2.77	-----	-----	-----	3.38	-----
	7. Oolong.....	45.1	2.93	-----	2.90	-----	3.22	-----
		46.2	3.29	-----	-----	-----	3.73	-----
A. L. Knisely, Portland, Oreg.	6. English Break-fast.	46.8	3.05	-----	3.19	-----	3.63	-----
		-----	3.15	-----	-----	-----	-----	-----
	7. Oolong.....	54.42	2.06	-----	1.95	-----	2.94	2.70
		54.75	1.74	-----	Lost.	-----	Lost.	-----
G. R. Stewart and A. R. Mehrtens, Berkeley, Cal.	6. English Break-fast.	48.76	1.92	-----	1.91	-----	3.16	2.93
		48.58	1.93	-----	1.74	-----	3.17	2.95
	7. Oolong.....	52.35	2.90	2.31	2.74	2.56	3.01	2.84
		52.30	2.92	2.44	2.63	2.52	3.00	2.88
	7. Oolong.....	47.24	2.99	2.90	3.30	3.06	3.36	3.24
		47.32	3.28	3.21	3.31	3.16	3.35	3.24
		-----	3.22	3.16	-----	-----	-----	-----
		-----	-----	-----	-----	-----	-----	-----

COMMENTS OF COLLABORATORS.

ON COFFEE.

J. A. Cummings: Commenting on the Gorter and the Lendrich and Nottbohm methods for the determination of caffein in coffee I would say that the Gorter method is the shorter, but it yields impure caffein, due to some colored substance which remains in solution after the cotton plug filtration. It was difficult in carrying out the Lendrich and Nottbohm method to get rid of the manganese dioxide by filtration, as some of it washed through the paper. It seems, too, that the carbon tetrachlorid extraction in this method yields a smaller percentage of caffein than does the chloroform extraction in the Gorter method. One explanation may be that the time for extraction in the Lendrich and Nottbohm method is not long enough for the complete extraction of the large amount of coffee used.

F. O. Woodruff: In the Doolittle and Woodruff method for insoluble extract much time is saved by a preliminary filtration through linen, after which the filtrate is warmed and passed through the tared paper, the insoluble residue being finally transferred to the tared filter and washed with repeated portions of hot water.

G. R. Stewart and A. R. Mehrtens: In this year's work on the coffee samples the Gorter method was found to be quite as satisfactory as before in regard to ease and rapidity of manipulation, but we believe that the results clearly show that the gravimetric determinations can not be taken as the final result in any case, owing to the impure caffein obtained. No good reason is therefore apparent for making this preliminary weighing, as it would be far more expeditious to transfer the chloroform extract directly to the Kjeldahl flask and proceed with the determination of the nitrogen. The results by the Lendrich and Nottbohm methods were, with one exception, obtained by a three hours' extraction with carbon tetrachlorid, as directed in the outline. The uniformly low amount of caffein extracted showed clearly that the three-hour period of extraction was insufficient. A six-hour extraction was therefore made on sample No. 4, Mocha coffee, and it will be observed that the result agrees closely with those obtained by the Gorter method. Unfortunately, lack of time prevented the repetition of the work on the entire series of coffees. It is, however, evident that either the time of extraction should be doubled or the amount of sample decreased to 10 grams, there being no reason why that amount should not be sufficient for an accurate determination.

The purity of the caffeine extracted by this method is clearly shown by the results obtained. It is believed that further work is warranted by this latter modification if it is desired to perfect a method which will yield satisfactory gravimetric results.

ON TEA.

G. R. Stewart and A. R. Mehrtens: In the Doolittle and Woodruff method for insoluble leaf great difficulty was experienced in completing the determination in a reasonable length of time. Between two and three days were consumed in filtering and washing the residue. For the sake of accuracy it was thought necessary to use S & S No. 575 hardened filters. Even these papers were completely disintegrated on subsequent drying, so that a considerable error appears to have been introduced from the continued solvent action of the hot water. It does not seem, therefore, that the method is workable in its present form.

In both the Doolittle and Woodruff and the Dvorkovitsch methods for the determination of caffeine in tea it was found that three extractions did not yield all the caffeine present in solution. Five portions of chloroform, consisting of 50, 25, 25, 20, and 20 cc, respectively, were used in the Doolittle and Woodruff method, and five portions of chloroform consisting of 100, 100, 75, 75, and 75 cc, respectively, in the Dvorkovitsch method.

It is felt that the modified Stahl Schmidt method is open to criticism on account of the appreciable error introduced by refluxing a measured volume from which an aliquot is afterwards taken, there being no way to absolutely prevent loss of water, which adheres to the condenser, stopper, and neck of flask. In other respects, facility of extraction, etc., this method was found to be a readily workable one.

RECOMMENDATIONS.

It is recommended—

(1) That the Gorter method for the determination of caffeine in coffee be further studied with a view to adopting it as official. The particular line of work referred to is the comparison of the gravimetric determination of caffeine with the result obtained by determining the nitrogen and multiplying by the factor 3.464, as it appears from the work here reported that the results by the gravimetric method are uniformly too high.

(2) That the Lendrich and Nottbohm method be further investigated. This further study would consist in modifying the method so as to use smaller samples—say, 10 grams instead of 20—and the time of extraction be increased, say, from 3 hours to 6 hours. The reason for further studying this method is because the purity of caffeine extracted by the Lendrich and Nottbohm method is very clearly indicated by the results obtained.

(3) That the Doolittle and Woodruff method as given in Bulletin 105, page 49, should be modified, as great difficulty was experienced by the different analysts in filtering and washing the residue.

(4) That the Doolittle and Woodruff method and the Dvorkovitsch method for the determination of thein and caffeine be further modified with reference to the number of extractions, as three extractions did not yield all the caffeine present.

(5) That since the modified Stahl Schmidt's method is open to criticism on account of the appreciable error introduced by refluxing a measured volume from which an aliquot is afterwards taken, a slight modification should be made to render this method readily workable.

(6) It is further recommended that no permanent changes be made in the methods until further study has been conducted along the lines indicated.

The following brief report was submitted by Mr. Mitchell at Mr. Barnard's request:

REPORT ON PRESERVATIVES.

By H. E. BARNARD, *Associate Referee.*

Early in the spring a circular letter was sent to each collaborating chemist requesting the following information:

- (1) Are any new preservatives being used in foodstuffs, as is constantly reported to be the case by rival manufacturing interests?
- (2) What preservatives are employed in foodstuffs?
- (3) Is the method for the estimation of benzoic acid satisfactory?
- (4) Is the method for the estimation of salicylic acid satisfactory?
- (5) Is the method for the estimation of borax satisfactory?
- (6) Do you consider saccharin to be a preservative?
- (7) Is beta-naphthol used as a preservative, and is there a satisfactory method for its estimation?
- (8) Are the fluorids used as a preservative and are there satisfactory methods for their detection?
- (9) Are the peroxids used as preservatives and are there satisfactory methods for their detection?
- (10) Along what lines can we best work?

From the responses to this inquiry, which was answered quite fully by each collaborator, I was able to tabulate the following data:

- (1) The methods employed for the estimation of benzoic, salicylic, and boric acid are satisfactory.
- (2) No new preservatives are being employed in the preservation of food-stuffs.
- (3) Beta-naphthol is not employed in the preservation of foodstuffs.
- (4) Saccharin, while not a true preservative, is, probably because of impurities present, of some value in inhibiting spoilage, and for that reason is classed by all the collaborators as a preservative.
- (5) The methods for the estimation of saccharin are not satisfactory.
- (6) Several collaborators express the opinion that the use of formic acid and its detection and estimation should be given attention.
- (7) One collaborator suggests that nitrates and sodium silicate sometimes used as a substitute for borax in ice-cream cones, and calls attention to the fact that methods for the examination of such products are not generally given.

These data were sent to all collaborators in August with the suggestion that their work should be directed to the development of definite methods for the detection and estimation of formic acid. Thus far no data have reached me, and it is not probable that any work of importance has yet been done along the lines suggested. In view of the facts developed through correspondence with collaborators and other food chemists, I am of the opinion that no more work is for the present necessary in the study of methods for the estimation of boric acid, salicylic acid, the fluorids, formaldehyde, and sulphurous acid. Investigations are still being continued with respect to benzoic acid and its salts, and the data should be reviewed by referees on the subject of food preservatives who may have charge of this work in the future.

REPORT ON WATER IN FOODS.

By HERMAN C. LYTGOE, *Associate Referee.*

It has been found by different analysts that in many cases there is a darkening of the sulphuric acid in the vacuum method of determining water in food. This is true of substances other than spices. H. C. Gore has found that the acid is to some extent volatilized and is found in the sample, possibly causing

some change in its composition. It is, therefore, recommended that the associate referee for 1912 make a study of the vacuum method, using different dehydrating agents.

METHODS OF ANALYSIS OF FRUIT PRODUCTS.

By A. E. PAUL.

The ordinary examination of jams and similar fruit products includes the following determinations: Solids, soluble, insoluble, and nonsugar; sucrose; reducing sugars; glucose; polarization, direct, invert, and at 87° C.; ash and its examination; acids; soluble phosphoric acid; preservatives and color. In following strictly the methods described in Bulletin 107, Revised, separate portions must be weighed out for the following: Solids, insoluble solids, reducing sugars, polarization, and ash. Reducing sugars are determined in a solution clarified with lead subacetate solution, while the polarizations are carried out with the use of normal lead acetate. In both cases the reagent is added to a solution which in most cases contains considerable free acid. Normal lead acetate solution under these conditions is entirely unsatisfactory. On the other hand, adding the subacetate to such a solution amounts to neutralizing the acidity of the fruit product with the lead solution before the reagent has any effect. By first neutralizing with sodium hydroxid, only a few cubic centimeters of the lead solution will be required. Minimizing the amount of lead used minimizes the amount of potassium oxalate necessary for its removal. This is important, for the reason that in inverting with hydrochloric acid an amount of this reagent equivalent to the potassium oxalate present will be rendered practically inert, it being replaced by an equivalent of oxalic and acetic acids.

The method for total solids is very unsatisfactory, and the modifications described in the Proceedings of 1910 leave the matter in an unsettled condition.

No method for determining phosphates is described for the class of substances under consideration.

Applied to jelly powders which usually contain large percentages of gelatin, the methods for polarization and sugars are practically useless. All of these difficulties are overcome by proceeding as follows:

JAMS, MARMALADES, FRESH AND CANNED FRUITS.

Preparation of sample.—Unless the container is very large, reduce to a pulp the entire contents by grinding in a large mortar. If the container is too large stir contents thoroughly and grind a suitable quantity. Two portions of this are used in the analysis, one for the determination and examination of ash, the other for all of the other determinations.

Ash; ash soluble in water; ash insoluble in water; alkalinity of soluble ash; alkalinity of insoluble ash; ash insoluble in hydrochloric acid.—Determine according to the official methods on the same 5 to 10 gram sample.

Insoluble solids.—Weigh 50 grams, stir in previously boiled, warm, distilled water, very gradually at first, then more rapidly, transferring to a 250 cc measuring flask, finally filling to the mark. Let stand at least one hour, shaking frequently. When cold, again fill to mark. Strain through a fine muslin, returning liquid to flask. Aliquots of this solution are used for all the determinations described below.

Wash insoluble material repeatedly and thoroughly upon the cloth, transfer to an aluminum dish provided with a cover and dry to constant weight in a jacketed steam oven. In each case, cover the dish before removing from the oven. Weigh quickly. Discard the washings.

Soluble solids.—Calculate from specific gravity of solution from insoluble solids, at room temperature, according to the tables in Bulletin 107, Revised, pages 66 and 67.

Acids.—Place 50 cc of the solution from the insoluble solids in a 100 cc measuring flask. Add phenolphthalein and titrate with tenth-normal sodium hydroxid.

Polarization direct; polarization invert; polarization invert at 87° C.; sucrose; glucose; nonsugar solids.—To the neutralized solution from "acids" add slight excess of basic lead acetate solution, Bulletin 107, Revised, page 40, and a little alumina cream. Fill to the mark, shake, and filter. Then proceed according to the official methods.

Reducing sugars.—Determine in 3 cc of the solution used for "Polarization direct," by Munson and Walker, Bulletin 107, Revised, page 242.

Soluble phosphoric acid.—To 50 cc solution add 1 cc of 10 per cent sodium hydroxid solution, evaporate to dryness and ignite at a dull red until practically all carbon is consumed. Dissolve in dilute nitric acid, and proceed according to Bulletin 107, Revised, page 3, near top.

Preservatives.—Extract 50 cc of the solution according to Bulletin 107, Revised; weigh the dried residue and divide into two parts. To one add ferric chlorid; to the other apply Heide and Jacob's modification of Mohler's test.

If necessary, repeat according to the provisional method described in Bulletin 137, page 111.

JELLIES.

Prepare sample as directed for "Jams, etc.," omitting directions under "Insoluble solids."

FRUIT JUICES.

Proceed as in the case of "Jellies," using the undiluted material or a suitable dilution, depending upon the consistency of the product.

GELATIN MIXTURES, JELLY POWDERS, ETC.

Sucrose.—In a 100 cc flask dissolve the normal weight of the product in about 50 cc water. Dissolve in about 25 cc water an amount of pure tannic acid equal to twice that of gelatin present. Add to the solution in the flask. Fill to the mark and shake. Filter through a loose filter until 50 cc have been obtained. To this, in a 100 cc measuring flask add 3 cc of lead subacetate solution (Bul. 107, Rev., p. 40) for each 1 gram of tannin present, a little alumina cream, and water to make 100 cc. Shake and filter. Free from lead with potassium oxalate, filter; polarize and calculate sucrose according to Clerget.

Gelatin.—Determine nitrogen by the Kjeldahl or Gunning method and calculate to gelatin, using the factor 5.55.

The following committee reports were made by Mr. Tolman, as chairman.

Standardization of alcohol tables.—It will be recalled that the tables approved by the committee and by the Bureau of Standards were provisionally adopted by the association last year, more definite action having been deferred pending the decision of the committee on revision of the Pharmacopœia. (Bul. 137, p. 48.) No action having been taken by the latter committee in the year past, no further progress can be made by the committee of the association at the present time, and it is, therefore recommended that the committee be discharged.

The report was received and the committee discharged as recommended.

Unification of methods of analysis of fats and oils.—It was found to be impossible to get a joint meeting of the various committees appointed on the standardization of methods by the different associations, but it is hoped that in 1912 at the meeting of the Eighth International Congress of Applied Chemistry such a joint meeting may be arranged by the collaboration of the sections of the congress, and the work be well organized. It is recommended, therefore, that the committee be continued.

The report was received and the committee continued as recommended.

As chairman of the committee on cooperation with other agricultural organizations, Mr. Wiley made the following report:

REPORT OF COMMITTEE ON COOPERATION WITH OTHER AGRICULTURAL ORGANIZATIONS.

By H. W. WILEY, *Chairman*.

The following resolution and agreement and the constitution proposed to effect the affiliation of societies interested in agricultural science are submitted for the information of this association:

A PROPOSED AFFILIATION OF SOCIETIES ORGANIZED FOR THE ADVANCEMENT OF AGRICULTURAL SCIENCE.

RESOLUTION AND AGREEMENT.

The authorized representatives of the associations and societies relating to agricultural science present at a meeting held in Washington, D. C., November 15, adopted the following resolution and constitution:

Resolved, That in order to promote common objects and interests there is special need of an affiliation of the various societies in North America which have for their objects the advancement of agriculture through scientific research:

That, therefore, the undersigned representatives of the Association of American Agricultural Colleges and Experiment Stations, American Association of Economic Entomologists, American Association of Farmers' Institute Workers, American Breeders' Association, American Phytopathological Society, American Society of Agronomy, American Society of Animal Nutrition, Association of Dairy Instructors, Association of Horticultural Inspectors, Association of Official Agricultural Chemists, Society for Horticultural Science, and Society for the Promotion of Agricultural Science hereby agree to affiliate under the following constitution, subject to ratification at the first regular session held by the societies mentioned subsequent to this date:

CONSTITUTION.

Article I. Name.

The name of this organization shall be the Affiliated Societies of Agricultural Science.

Article II. Purpose.

The purpose of the affiliation shall be to promote the common interests of the adhering societies, arrange periodically for a common place and time of meeting, promote economy and efficiency in publications, and otherwise to encourage cooperation in the advancement of agriculture through scientific research.

Article III. Membership.

The organization shall consist of national societies which have for their prime object the advancement of agriculture. The societies mentioned in the accompanying resolution shall be charter members. Additional societies may be admitted at any general meeting of the affiliated societies.

Article IV. Organization.

The general business of the organization shall be in charge of a council to consist of one member elected biennially by each adhering society.

The officers of the council shall be a president, a vice president, a secretary, and a treasurer, who shall serve for six months after their successors are elected. These officers shall constitute the officers of the organization.

Article V. Meetings.

A general meeting of the affiliated societies shall be held at least biennially, at a time and place to be determined by the council. Any adhering society may hold meetings at such times and places as it may select, but so far as practicable all should meet together biennially.

Article VI. Autonomy.

Each society shall retain its organization and shall have entire control of the election of its members and officers and all other matters not specifically delegated by it to the council of the affiliated societies.

Article VII. Annual dues.

Each society upon becoming a member of the organization shall pay to the treasurer of the council a pro rata sum, not to exceed \$1 for each of its members, and a similar amount thereafter annually, the amount in each case to be fixed by the council. The fiscal year of the affiliated societies shall coincide with the calendar year.

Article VIII. Publications.

The Proceedings of the various societies may be issued individually, but all should conform to a uniform style of page, paper, and type, in order that they may constitute uniform parts of a set of Transactions of the Affiliated Societies.

The council may, upon the approval of the adhering societies, superintend the publication of their Proceedings and employ a general editor to cooperate with the editors of the various societies in securing uniformity, economy, and efficiency.

The council may arrange for the periodical publication of a journal of agricultural science, to contain reports in abstract of the meetings of the societies, brief notices, reviews, and contributions of general interest to the members of the affiliated societies and for the interchange of ideas on important problems of the day relating to agricultural science, this journal to be issued to members at a subscription price to be fixed by the council.

Article IX. Amendments.

Amendments to this constitution may be made at any general session of the affiliation upon the recommendation of the council, provided that 60 days' notice of the proposed amendments has been given to the president and secretary of the adhering societies.

Article X. By-laws.

The council shall formulate and adopt a set of by-laws to govern its actions under this constitution.

It will be seen that the proposed affiliation affects in no way the organization of the separate societies and would seem to be of value in unifying the work. Only one section of the constitution calls for special consideration, namely, Article VII, on annual dues. I recommend on behalf of the committee that the report be referred to the executive committee of the association, with power to act, except that they shall not enter into any financial agreement before reporting to the association at the next meeting.

The report was accepted and the recommendation adopted.

PRESIDENT'S ADDRESS.

By F. W. WOLL.

The present convention is the twenty-eighth annual meeting which our association has held. As we look back upon the work accomplished in the past it is a source of great satisfaction to be able to feel that our association has been a most important factor in the development of agricultural chemical analysis and of agricultural science in this country. All who are conversant with the conditions as they existed in the early eighties and as they are to-day know that this statement is fully justified. Looking back to the former period, we find, in the words of our secretary, that "the few chemists who were engaged in agricultural research were acting in complete independence of each other in regard to methods of investigation and of research. Some of them were using the methods employed by German chemists, while others followed the instruction given by the French or English agricultural chemists. There was no unity of interest in the profession, nor any common system of work. The condition of analytical work may be truly described as chaotic. The result of such condition is easily imagined. There was no standard of comparison or reference. Buyers and sellers were continually wrangling over analyses which, made by different men following different methods, did not agree. The sellers' chemists uniformly obtained higher results than the buyers', and thus the door of litigation was constantly open."¹

The difference between the past and the present is marked all along the line. We can not point to one of the criticisms of the conditions as they existed that is not practically removed at the present time, and the credit for the progress made belongs largely to our association. It has been the central force that has made the progress and improvement in the methods of analysis and of research bearing on agricultural chemical problems, and in the relations of our agricultural chemists to each other and to their brethren engaged in industrial work. Hence we may have a pardonable pride at the contemplation of the work which our association has been able to accomplish within the relatively short period that it has been in existence and think with gratitude of the men who have been the leaders in this work and are largely responsible for the progress that has been made. Of the small band of agricultural chemists who were prime movers in the organization of this association, a large majority have now gone to their reward and but few are still actively engaged in the work to which they have devoted the best efforts and energies of their lives. Most of the present membership of our association belongs to the second generation, who received their college or other preparatory technical education during the first decade or two after this association was organized. As they may not, therefore, be especially familiar with the early history of the association a few words along this line may not be amiss.

Although our association officially dates back to 1884, when the organization was effected and the constitution adopted, there had been held four meetings prior to that date, by eastern or southern chemists interested in the study and further development of methods of fertilizer analysis. The first meeting was held in Washington, 1880, in response to a call signed by the Hon. J. T. Henderson, commissioner of agriculture of Georgia, and issued at the request of former Director Redding, of Georgia Experiment Station, while the following meetings were held in Boston (also in 1880), in Cincinnati in 1881, and in Atlanta in 1884. Out of the Atlanta meeting grew the organization of our present association at the meeting held in Philadelphia, September 8 to 9, 1884.

¹ U. S. Dept. Agr., Division of Chemistry Bul. 57, p. 16.

The objects of the association, according to the constitution adopted at that meeting, were twofold—(1) to secure as far as possible uniformity in legislation with regard to the regulation of the sale of commercial fertilizers in the different States, and (2) uniformity and accuracy in the methods and results of fertilizer analyses. It soon became clear to all that the primary usefulness of the association lay in the direction of studies and comparisons of methods of analysis rather than in influencing legislation with regard to the regulation of the sale of commercial fertilizers in different States, and during the past quarter of a century the work of the association has been almost wholly in the former direction. The main and about the only direct result accomplished in a legislative line was the adoption of the report of the special committee with regard to a uniform fertilizer law in 1898.

The association was organized for the purpose of studying methods of analysis of phosphoric acid, nitrogen, and potash, but its work was only confined within these narrow limits for two years. As early as 1886 Commissioner of Agriculture Norman J. Colman, in a letter to the executive committee, suggested that it would be both wise and profitable to widen the scope of the investigations conducted to include other subjects than those immediately connected with the analysis of fertilizers, and the president of the association that year, our present secretary, in his presidential address likewise urged an extension of the character of the work to be undertaken. "Every problem," he says, "connected with chemical agricultural analysis falling within the range of the studies of anyone connected officially with the agricultural interests of the country seems to me to be a proper theme for our discussion here. Thus all the problems relating to the adulteration of food, the general method of agricultural analysis, and all other matters which concern, in common, the analyst and the public, could be included among the duties and privileges of this body."

Other subjects have as a result been added to the list of materials for which methods of analysis were to be studied and discussed by our association. First came cattle foods and dairy products in 1886; then, in 1887, fermented liquors and sugar; 1890, soils and ash; 1894, tannin; 1897, liquor and food adulteration; 1898, insecticides; 1901, food adulteration (with 17 associate referees, which by this time has been increased to 30); 1903, medicinal plants and drugs; 1904, inorganic plant constituents; and in 1908, water, until at the present time it may be truthfully said that our work more than covers the entire field of agricultural chemical analysis as outlined by our secretary 25 years ago.

Our association is unique in several ways: It is the largest body of agricultural chemists in the world and has a wider scope than any of the foreign societies organized for similar work. It has been its good fortune to have the cordial support of our National and State agricultural institutions of research and instruction, and through the cooperation of the United States Department of Agriculture our worthy secretary has been able to serve the association as president, member of the executive committee, and in his present capacity, for an unbroken series of 28 years. The history of the Association of Official Agricultural Chemists, with Dr. Wiley left out, would be like Shakespeare's Hamlet without "the melancholy Dane," and I imagine that when his (Wiley's) labors are ended and his biographers pass in review the story of what he accomplished, they will accord a very prominent place to his faithful and efficient connection with our association; and let it be a consolation and satisfaction to him to know, amid all abuse, ridicule, and misrepresentation from special interests, from whose adulterated products of all kinds he has protected God's poor, the patient and long-suffering public, that his work in our association and in the interest of pure food, drink, and drugs is duly

appreciated by our members and by the general public through the length and breadth of our land. They know, as we know, that he has fought their fight courageously, honestly, and with unflinching fidelity. [Applause.]

Our association is unique in another way. By our laws of organization and established custom we have now a staff of over 50 referees and associate referees who each year plan cooperative work in their respective lines and prepare reports on the work connected with analyses of special substances. Each one contributes what he can toward the study and perfection of these methods or works out new methods by which our knowledge of the chemical analysis of materials coming within the range of the association may be enlarged and greater accuracy of results obtained. This splendid permanent organization for work which we thus possess makes a most valuable asset and has been of the greatest benefit to the chemists of our country, as well as to the referees and the associate referees themselves and their collaborators. It makes the work of the officers of the association in preparing the programme of the convention largely perfunctory. There is probably no set of officials in a national organization of the importance or membership of this association who have an easier task in this direction than have your officers. No solicitation of papers here or urging attendance or participation in discussions. The president calls the meeting to order and appoints a few committees, and the referees and associate referees do the rest.

It is easily seen that this organization of the work of the association has its weaknesses as well as its advantages. The mere fact that so many take part in the programme may dampen the ardor of some, and there is also a danger that the similarity of the reports presented and the somewhat stereotyped plan of cooperative work undertaken in many lines may tend to lessen the interest of some members in the work of the association and in the proceedings of our convention. The extreme specialization which is inevitable under present-day conditions also renders it difficult for some chemists to follow with profit the reports and discussions in fields of chemical analysis far removed from those in which their own special work generally lies.

There can be no doubt, however, that participation in the cooperative work of the association offers an excellent opportunity for study of special methods and for comparing one's own results and working methods with those of other chemists. Many an error of analysis has been discovered in the past, and faulty methods of manipulation have been corrected, through the check furnished by the collaboration of chemists working with samples of the same origin and under the same specific directions. One suggestion may be made in this connection, that referees arrange to have a sufficient number of copies of the compilation of the results obtained in the year's work to supply them by mail to all chemists who have cooperated with them, thereby giving those who are not so favored by geographical location or a good-sized pocketbook that they are able to attend the meetings regularly, an opportunity to find out, while the work is fresh in their minds, how their results compare with those of other chemists. Another advantage would be that chemists could then go over the work again early in the fall in case it should prove desirable to do so, before instructional or research work once more demands all their time and energies.

A suggestion may be in order with reference to the cooperative work planned. Referees sometimes forget that most collaborators are busy men, whose working hours are wholly taken up with the work for which they receive their modest allowance, and more cooperative work is often requested than can be done by a chemist during a period of several weeks. The result is that many are discouraged from taking part in the work at all. If each referee asked for coop-

eration with regard to only a couple of points, more chemists would feel disposed to undertake the work than is now often the case, and the returns would be of more value both to the referee and to the association. A small step in advance along the whole line each year will bring more satisfactory results, and we shall progress faster and farther than if too much is attempted. If referees and associate referees on the respective subjects will confer carefully beforehand regarding the points to be studied and bear in mind the suggestion just made, there will not be much occasion for apologies in the reports on cooperative work presented, and each year will see decided progress made toward more satisfactory methods of analysis.

Active participation in the work of the association is not only important and an inspiration to the individual chemists who plan or carry it through—the institutions they represent and their directors are benefited to a similar extent. During the last 12 years the chemical control work that our institutions are called upon to do has widened in scope, and nearly all now have duties along one or more lines of inspection. The fertilizer control work, as you all know, came first, then came feeding stuffs, and of late insecticides and fungicides have been added to the list, so that most of us may now be called upon at any time to prove the correctness of the analytical work done with these materials, either before the courts or to our friends the commercial chemists, or those employed by manufacturing firms.

While we all feel the responsibility of our position, and do not report results until we have full confidence in their correctness, mistakes will occasionally occur in spite of all care, and the annual checking up of methods and results afforded by the cooperative work of this association here comes in as a comfort and an aid. We find our own results corroborated by chemists working with the same materials but under widely differing conditions, often with minor differences in regard to details of manipulation, and with different standard solutions, chemicals, balances, and weights. Our confidence in the work of our laboratory and in ourselves is thus strengthened, or, if errors are discovered, we are led to look for and correct them, with a very pleasant feeling of satisfaction resulting. For this reason it would seem we can well afford to give up a week or more, if necessary, of our own or our men's time each year to do the cooperative work planned along the lines of activities in which our laboratories are directly interested. It is good for our chemists, it is good for our institutions, and it is good for our association, whose work is advanced nearly in proportion to the number of chemists cooperating under the guidance of able referees and associate referees who are specialists in their respective lines of study.

The danger of overspecialization is with us always, in chemistry as elsewhere, and those responsible for the training of young chemists can not emphasize too strongly the necessity of a thorough fundamental knowledge of general chemistry and chemical analysis before specialties are taken up. The broader and more solid foundation the chemist brings to his chosen work the better position he will be in to grapple with the problems which this presents, the more valuable his services will prove to his employers, and the better are his chances of rising above the level of the average, in reputation and in the emoluments a useful man can command. In addition to a thorough fundamental training the cardinal virtues of care, honesty, and accuracy in the conduct of one's work are primary requisites, without which no chemist can hope to win recognition.

The story is told of Bunsen that while making a quantitative analysis of some material at one time he was unfortunate enough to upset the beaker in which the solution was heated, and spilled some of it on the laboratory table. With the ever-present German laboratory sponge he wiped the table and

squeezed the sponge over the beaker. A similar mishap occurred again a little later and the difficulty was remedied in the same way, the famous chemist mumbling to himself as he squeezed the solution into the beaker the second time, "Oh, pshaw! if that happens once more I shall have to begin all over again." The story, if true, only illustrates that a man may be a great scientist and discoverer without being a good analyst. For the large majority of us who are not by nature endowed with marked ability to discover new paths in science, or to enlarge in a brilliant way the sum of human knowledge, the safer plan, by far, is to do well what we can do, so that our results will bear the severest scrutiny and we may have the satisfaction of knowing that they can be corroborated by carefully trained chemists everywhere, irrespective of geographical location, nationality, or position.

As suggested at the outset, the work of the association in the past has been of the greatest service to the chemists of our country and elsewhere, as well as to our agricultural interests in general. Our methods of analysis have been closely studied, and those proving the most accurate and satisfactory have been given official stamp after continued careful investigation and scrutiny. Much progress has thus been made, and, while the best of to-day may not stand the test of to-morrow or the day after, we believe that along most lines of analytical work in which we are interested the methods now at our disposal will stand the test of time and will require further study only in regard to details of manipulation. Along other lines, however, much still remains to be done before we can feel that this goal has been reached, and in order to reach it we shall need the hearty cooperation and the best assistance of all members in their respective fields of study. Our experience in the past and the character of our present large membership justify the confident hope that the importance of our association and its usefulness to the chemical profession and to agricultural science will prove still greater in the future than has been the case in the past, and that it will receive the cordial support of all members in solving the problems confronting it now and in the future, the work being characterized by the same spirit, enthusiasm, and energy as have overcome difficulties and aided us in gaining a clearer knowledge in the past.

TUESDAY—AFTERNOON SESSION.

REPORT ON THE SEPARATION OF NITROGENOUS BODIES (MEAT PROTEIDS).

By C. R. MOULTON, *Referee*.¹

The cooperative work done this year on the separation of meat proteids has been limited to the determination of total nitrogen in concentrated beef extracts. The lack of agreement among the analysts in this work during the past two years, on the one hand, and, on the other hand, the contention by some that the official methods are satisfactory led the referee to make a further test of the methods for total nitrogen.

The samples of concentrated beef extract employed were the same as those used in our previous work,² and were prepared in the laboratories of the Missouri agricultural experiment station. The samples showed a large amount

¹ Presented by P. F. Trowbridge.

² Sample 1 was sent to J. T. Willard, E. B. Forbes, A. D. Emmett, Paul Rudnick, and A. Lowenstein. Sample 2 was sent to T. C. Trescot and T. L. Haecker.

of crystalline bodies which settled out on standing. It was suggested that, in order to remove any errors which might arise from this source, the sample be very thoroughly mixed and a large sample be weighed out by the method of difference, dissolved in water, filtered, and made up to a volume. Aliquots for total (soluble) nitrogen could be drawn from this solution. This, of course, gives soluble nitrogen, but it affords a good comparison for the method for total nitrogen and removes any error due to lack of uniformity of sample. Letters were sent to 22 laboratories, and 7 men signified their ability to cooperate.

REPORTS OF REFEREES.

J. T. Willard reports the work of J. W. Calvin as follows:

Nitrogen determination.—Two charges were weighed out as directed, dissolved in water, and made up to volumes of 250 cc. Two portions of 25 cc each, or one-tenth of the charge, were taken from each solution and digested with 0.7 gram of mercury and 30 cc of sulphuric acid for three and one-half hours, although the liquid was colorless after the end of the first hour. The following results were obtained: Charge 1: 6.7050 grams, aliquot 0.6705; per cent nitrogen, 8.755, 8.725. Charge 2: 7.2782 grams, aliquot 0.7278; per cent nitrogen, 8.759, 8.759.

R. C. Collison reports upon the sample sent to E. B. Forbes as follows:

About 10 grams of the well-mixed sample were weighed by difference into a Kjeldahl flask; 50 cc of sulphuric acid and 0.6 gram of metallic mercury were added. The contents were digested for about one hour or one and one-half hours and 10 grams of potassium sulphate added. The digestion was continued until the solutions were practically clear. Total time of digestion, six hours. The solution was then made up in a volumetric flask and an aliquot distilled in the usual way. Results: 8.74, 8.73, 8.75, 8.80; average, 8.755 per cent.

Another sample of about 10 grams was dissolved in water made up in a volumetric flask and an aliquot digested as before, using 20 cc of sulphuric acid, 0.6 gram of mercury, and 10 grams of potassium sulphate. The whole aliquot was distilled. Percentage results on nitrogen by this method: 8.74, 8.80; average, 8.77 per cent.

A. D. Emmett reports as follows:

The sample was digested at a low temperature until the frothing ceased. This generally occupied from 15 to 20 minutes. The 5 grams of potassium sulphate and 0.65 grams of mercury were then added. The digestion was continued until the mass became clear, which took varying lengths of time, as shown in the table. The heat was turned off as soon as the digest became clear, and the neck of the flask was then washed down, after which the digestion was continued for one and one-half hours. Then 250 cc of ammonia-free water were added, a small amount of pumice, and the customary amount of potassium sulphid and sodium hydrate. The distillation was carried out so that 250 cc of the distillate came over in about 35 to 40 minutes. The indicator used was Congo Red, the standard acid was hydrochloric, and the alkali, sodium hydroxid. Blank determinations were run on all reagents and the correction applied for these in making the final calculations. We made the determinations on both unfiltered and filtered samples. The data seem to indicate that with the exception of test "A" one can obtain fairly satisfactory results by the method just outlined, both for the filtered and unfiltered samples.

Nitrogen results by A. D. Emmett on filtered and unfiltered samples.

Test number.	Total amount taken.	Total volume.	Volume taken.	Time of digestion.			Nitrogen.	
				Until clear.	After clear until end.	Total.	Unfiltered.	Filtered.
	<i>Grams.</i>	<i>cc.</i>	<i>cc.</i>	<i>Hr. min.</i>	<i>Hr. min.</i>	<i>Hr. min.</i>	<i>Per cent.</i>	<i>Per cent.</i>
A 1.....	10.1044	250	25	0 55	1 30	2 25	8.80	8.41
2.....							9.04	8.67
3.....							8.80	8.22
Average.....							8.87	8.43
B 1.....	9.4593	250	25	1 15	1 30	2 45	8.65	8.54
2.....							8.65	8.47
3.....							8.65	8.46
Average.....							8.65	8.49
C 1.....	7.6605	250	25	1 05	1 30	2 35	8.55	8.50
2.....							8.65	8.53
3.....							8.65	8.43
Average.....							8.60	8.49
D 1.....	5.4064	250	25	0 50	1 30	2 20	8.65	8.55
2.....							8.67	8.50
Average.....							8.66	8.53

Paul Rudnick makes the following report:

We find in this laboratory that the quantity of extract to be digested must not exceed 0.85 gram, and should probably be less than this in order to get concordant results; the time of digestion is fixed at two hours after the digestion comes to final color, and never less than three hours in all, and the method employed is the so-called combination Kjeldahl-Gunning method, using 5 grams of potassium sulphate and 0.5 gram of metallic mercury.

Nitrogen results reported by Paul Rudnick.

Solution.		Weight of sample.	Time of digestion.	Nitrogen.
		<i>Grams.</i>	<i>Hours.</i>	<i>Per cent.</i>
50 cc:				
1A.....		0.9764	3	9.22
1B.....		.9764	3	9.25
2A.....		.9914	3	8.97
2B.....		.9914	3	8.99
3A.....		1.0226	3	8.87
3B.....		1.0226	3	8.89
100 cc:				
1C.....		1.9527	3	9.27
2C.....		1.9828	3	8.97
3C.....		2.0452	3	8.92
1, 2, 3, D.....		1.9957	3	8.71
1, 2, 3, E.....		1.9957	3	8.97
4A.....		3.8428	5	8.64
5A.....		4.4015	5	8.13
150 cc:				
4B.....		5.7643	9	8.61
5B.....		6.6022	9	8.24

The solutions were made up in accordance with your suggestion to weigh approximately 10 grams by difference, dissolve in water, filter, and make up to volume. The weights were taken and the solutions made up as follows:

Description of solutions.

Solution No.	Beef extract.	Volume of finished solution.
	<i>Grams.</i>	<i>cc.</i>
1.....	9.7635	500
2.....	9.9140	500
3.....	10.2262	500
4.....	9.6071	250
5.....	11.0037	250

In the table of results the figures in the first column refer to the number of the solution, while the letters serve to distinguish the successive aliquot portions from each solution. The results marked 1, 2, 3, D, and 1, 2, 3, E, respectively, were drawn from composite solutions made up from equal volumes of solutions 1, 2, and 3.

Nitrogen was determined in all cases by the so-called Kjeldahl-Gunning method, using 5 grams of potassium sulphate, 0.5 gram of metallic mercury, and 25 cc of sulphuric acid. Blanks were deducted in each case as usual, amounting in this case to 0.0007 gram of nitrogen, and the results reported are those obtained after correcting for this blank.

The results show clearly the tendency toward lower results, with larger samples, in spite of increased time of digestion. It seems highly probable that this is due to the same cause which produces the tendency toward low results in commercial ammoniates of high nitrogen content, such as dried blood, tankage, etc., when the time of digestion is too short. Whether this is due to the formation of organic amines or amino acids, etc., which do not react with the indicator as equivalents of ammonia is an interesting question. So far as I know, it is commonly assumed among analysts that the oxidation of the nitrogen compounds in this determination proceeds quantitatively until all the nitrogen is present as ammonium salts, but it does not seem to me that this view can be correct.

It may be of interest to you to know the results obtained on determining nitrogen in the papers through which the above solutions were filtered:

Nitrogen found in filter papers used in preceding determinations. (Rudnick.)

Solution.	Weight of sample.	Nitrogen.
	<i>Grams.</i>	<i>Per cent.</i>
1.....	9.7635	0.10
2.....	9.914	.08
3.....	10.2262	.07
4.....	9.6071	.07
5.....	11.0037	.06

The same sample was analyzed in the Missouri laboratories by E. E. Vanatta. The Kjeldahl-Gunning method was employed, using 30 to 35 cc of sulphuric acid and 0.7 gram of metallic mercury. This was digested until the sample was no longer "pasty," when from 5 to 7 grams of potassium sulphate were added. The digestion was continued until the sample was colorless, when the neck of the flask was washed down with water and the digestion was continued. The aliquots given in the table were used for digestion. Twenty-five grams were dissolved in water, filtered, and made up to 1,000 cc.

Report on sample 1, by E. E. Vanatta.

Solution and aliquot.	Hydrochloric acid.	Nitrogen.	Weight sample.	Time.		
				Before clearing.	After clearing.	Total.
10 cubic centimeters:	cc.	Per cent.	Grams.	Min.	Min.	Hr. min.
A 1a.....	16.67	8.362	0.25	25	30	0 55
b.....	Lost.			30	0 55
2a.....	16.77	8.412			60	1 25
b.....	16.88	8.467			60	1 25
3a.....	16.67	8.362			120	2 25
b.....	Lost.			120	2 25
20 cubic centimeters:						
B 1a.....	33.45	8.389	0.50	25	30	0 55
b.....	Lost.			30	0 55
2a.....	33.43	8.384			60	1 25
b.....	33.55	8.414			60	1 25
3a.....	33.60	8.427			120	2 25
b.....	33.53	8.409			120	2 25
35 cubic centimeters:						
C 1a.....	58.30	8.355	0.875	35	30	1 5
b.....	58.75	8.420			30	1 5
2a.....	58.85	8.434			60	1 35
b.....	58.75	8.420			60	1 35
3a.....	59.05	8.463			120	2 35
b.....	59.03	8.460			120	2 35
100 cubic centimeters:						
D 1a.....	167.28	8.391	2.500	55	30	1 25
b.....	Lost.			30	1 25
2a.....	171.12	8.583			60	1 55
b.....	171.48	8.601			60	1 55
3a.....	169.83	8.519			120	2 55
b.....	171.53	8.604			120	2 55
Average.....		8.444				

Mr. Lowenstein writes as follows in regard to this work:

In this connection we were very much interested in the report which you submitted to the association, as printed in Bulletin 137, Bureau of Chemistry. We note that you state that you had "some difficulty in getting good duplicate results for nitrogen in the case of beef extracts when samples of about 2 grams were weighed out for total nitrogen and digested by the modified Kjeldahl method." We have used this method in our laboratory for a long time and have never experienced any such difficulty as you mention, even when the work was done by men who have had very little experience in analytical work. In the attached analysis Analyst B has had only two months' experience in commercial analytical work. We could cite numerous instances of analyses run by this method, in all of which our duplicate results have been as close as in the attached, and we know of no instances where we have had any such results as appear in your report.

We thought at first that your trouble might have been due to the sample, as in our ordinary run of commercial work we very rarely run across a sample of beef extract such as submitted by you. However, we have been able to get good duplicate results from the sample submitted within our own laboratory. We will be very much interested to see the cooperative results on this sample.

The sample submitted was run by the method suggested in your letter and also by the modified Kjeldahl method, two grams of the sample being used for the determination.

Nitrogen results on official sample by two methods.

Modified Kjeldahl method.		Moulton method.	
Analyst A.	Analyst B.	Analyst A.	Analyst B.
Per cent.	Per cent.	Per cent.	Per cent.
8.93	8.92	8.98	8.89
8.90	8.90	8.99	8.85

Our method of digesting the sample, in detail, is as follows:

Two grams of the sample are weighed in a tared filter paper and the entire sample is put in a Kjeldahl flask. One-half gram of metallic mercury and 10 grams of crystalline potassium sulphate are then added together with 25 cc of concentrated sulphuric acid. The sample is then digested for three hours, after which with the addition of a little zinc dust and a few drops of paraffin oil and 350 cc of water, together with 50 cc of caustic soda solution containing the proper amount of potassium sulphid, it is distilled into a 500 cc Erlenmeyer flask containing 25 cc of standard hydrochloric acid (1 cc equals 1 per cent ammonia where a 1 gram sample is employed).

The analytical work on this sample was done by J. J. Vollertsen and an assistant, to whom credit is due.

On sample 2 T. C. Trescot reports as follows:

Results on sample 2 by the Gunning method, varying size of sample.

Weight of sample.	Total nitrogen.
<i>Grams.</i>	<i>Per cent.</i>
1.7382	8.73
1.2974	8.71
1.9235	8.66
1.9702	8.77
0.2395	8.67

The digestion was continued four hours. This is the usual method for determining nitrogen in meat extract in this laboratory. Following the suggestion of the referee, we dissolved 20 grams of the extract in 200 cc of water, filtered and determined the nitrogen in 10 cc portions of the filtrate. The results were as follows: Weight of sample, 1 gram; per cent of soluble nitrogen, 8.28 and 8.22.

In order to check the work upon the referee's sample, we determined the nitrogen in a sample of Liebig's extract with the following results: Weight of sample, 1.8820 grams; per cent of nitrogen, 9.54; 0.9578 gram, 9.55 per cent; 0.9578 gram, 9.49 per cent, and 0.9578 gram sample, 9.49 per cent nitrogen. In this work the time required for a sample to become clear on digestion was by no means constant. The length of time required depended largely upon the size of the sample.

The size of the sample seemed to have no influence upon the percentage of nitrogen.

T. L. Haecker reports the work from the Minnesota laboratory by Mr. Anthony as follows:

Nitrogen results on referee's samples as reported by Haecker.

Beef extract samples.	Weight of sample.	Aliquot parts taken for digestion.	Total time of digestion.	Hydrochloric acid used.	Soluble nitrogen.	Remarks.
	<i>Grams.</i>	<i>cc.</i>	<i>Hours.</i>	<i>cc.</i>	<i>Per cent.</i>	
1.....	12.8864					Dissolved in H ₂ O and made to 500 cc.
1-a.....		50	5½	33.89	8.641	Digested with K ₂ SO ₄ and HgO.
1-b.....		50	5½	33.81	8.621	Do.
Average.....					8.631	
1-c.....		50	5½	33.82	8.623	Digested with HgO only.
1-d.....		50	5½	34.07	8.687	Do.
Average.....					8.655	
1-e.....		10	5	6.70	8.542	Digested after Milbaur's method.
1-f.....		10	5½	6.69	8.530	Do.
Average.....					8.536	

Nitrogen results on referee's samples as reported by Haecker—Continued.

Beef extract samples.	Weight of sample.	Aliquot parts taken for digestion.	Total time of digestion.	Hydrochloric acid used.	Soluble nitrogen.	Remarks.
	<i>Grams.</i>	<i>cc.</i>	<i>Hours.</i>	<i>cc.</i>	<i>Per cent.</i>	
2.....	5.4521	8				After digestion made to 500 cc, digested with K_2SO_4 and HgO .
2-a.....			50	14.28	18.605	
2-b.....			50	14.33	8.636	
Average.....					8.62	
3.....	4.4171	8				Do.
3-a.....			50	11.29	18.398	
3-b.....			50	11.23	8.353	
Average.....					8.375	

¹ Total nitrogen.

Comments on this work made by Mr. Haecker are as follows:

From the thoroughly mixed substance three individual samples were weighed out by the method of difference.

Sample No. 1, weighing 12.8864 grams, was dissolved in a beaker with water, filtered, and made up to the volume of 500 cc at 15° C. From this solution, four aliquot parts of 50 cc each (1-a, 1-b, 1-c, 1-d) were drawn for digestion. To samples 1-a and 1-b 10 grams of potassium sulphate and about 0.7 gram of mercuric oxid were added; to samples 1-c and 1-d only about 0.7 gram of mercuric oxid.

The digestion was carried on, first, with a low flame until most of the water was evaporated and the sulphuric acid fumes began to rise, then potassium sulphate and mercuric oxid were added and the digestion carried on *for four hours after the solution became colorless*. The distillation of the samples was carried out as usual, with the only difference that the boiling was slow and the whole process of distillation continued for about one hour and a half. An excess of standard hydrochloric acid was used to catch the distillate, and a corresponding potassium hydroxid solution with cochineal as an indicator was used for titration.

Two blanks were run with about 1 gram of chemically pure anhydrous lactose ($C_{12}H_{22}O_{11}$) using the modified Gunning method for digestion. The correction of 0.5 cc of hydrochloric acid used was equally applicable to all analyses.

Sample No. 2, weighing 5.4521 grams, and sample No. 3, weighing 4.4171 grams, were placed in Kjeldahl flasks and digested after the modified Kjeldahl-Gunning method. The heating of the substance was slow, and the digestion was continued *for six hours after the substance became colorless*. The digested samples were made up to 500 cc at 15° C., and 50 cc duplicates were drawn for distillation. The distillation was carried on as with sample No. 1.

The results obtained by either method show a marked check in the duplicate analyses and between each other. A discrepancy of only 0.25 per cent occurs between sample No. 2 and sample No. 3. This discrepancy I think can be credited to an analytical error or to the fact that the last sample did not correspond to the average, because of the accumulation of small crystals in the bottom of the weighing glass.

Discrepancies in the nitrogen content of a larger and a smaller sample should be credited only to an incomplete digestion or to an error in the process of distillation. Larger samples correspond better to the average than small samples. Even if duplicate small samples of 0.5 gram would check closely they do not give us a guarantee of an average result. Larger samples, however, check equally well, and the results come the nearest to the average composition of the material.

The distillates obtained were clear and no difficulty with the indicator could be noticed in the titration.

To test whether the amido nitrogen is completely hydrolyzed by the common Kjeldahl method Milbaur's modification as applied to hydrazones and osazones

was used. The two results obtained check exceptionally well, but, of course, from only two determinations no conclusions can be drawn.

The method of Milbaur was used in the following way: 10 cc of the liquid sample were measured from a burette into a Kjeldahl flask; 40 cc of water and 50 cc of concentrated sulphuric acid were added; 3 grams of powdered chemically pure zinc previously washed in 1 per cent sulphuric acid were poured into the flask. The contents were previously cooled to prevent a too strong reaction. The substance was heated very slowly over a wire gauze, and the heating continued until no more hydrogen was generated. The generation of hydrogen ceased after one-half hour and then two drops of metallic mercury were added and the digestion carried on as usual. After the substance became white it was left to cool a little, and 1 gram of chemically pure potassium dichromate was added and the digestion carried on for two hours longer. Milbaur uses 2 grams of potassium persulphate, but since this was not at hand the dichromate was used instead. The solution was distilled from a copper flask to prevent bumping. [In this connection the referee wishes to call attention to results obtained two years ago in the Missouri laboratory on the same sample—total nitrogen on 2-gram samples, 9.341 and 9.474 per cent; soluble nitrogen on 0.5-gram samples, 8.389 and 8.731 per cent.]

DISCUSSION.

A study of the foregoing data shows rather marked uniformity in the results on total nitrogen. On sample No. 1 the three investigators report results between 8.7 and 8.8 per cent of total nitrogen. Good duplicates are obtained by different chemists. Two of the investigators get rather higher results, averaging rather close to 9 per cent. Comparing insoluble nitrogen in this sample, the figures submitted by Mr. Emmett are exceedingly good duplicates of the figures obtained in the Missouri laboratory. In connection with the higher results obtained by the two collaborators in the stock yards, the following extract from Mr. Rudnick's report is of interest: "I should like to comment upon the data obtained in the determination of nitrogen on the water-insoluble residue remaining on the filters. These filters were well washed and no trace of yellow color was visible on them. It would seem, therefore, that the crystalline water-insoluble substances may possibly contain crystalline meat bases or other nitrogenous organic compounds in addition to inorganic solids. I regret that lack of material and time did not permit a further investigation of this question, which might throw some light on the discrepancies in the determination of nitrogen in beef extracts."

At the Missouri station we had no trouble in getting crystalline bodies into solution provided the sample was allowed to stand covered with water for 15 or 20 minutes before filtering. The residue on the filter papers in filtering out the insoluble nitrogen had the appearance of a brownish coagulum and no crystals were left.

Turning our attention to sample No. 2, it is seen that the two collaborators obtained results for total nitrogen that agreed very well. Their results on soluble nitrogen do not show the same agreement, but this may be accounted for by insufficient oxidation or some other error in the method. In this work the collaborators used almost exclusively the so-called Kjeldahl-Gunning method. Following the referee's suggestion that the best method be selected, they have, with two exceptions, used this method. It therefore seems to the referee that when care is taken to get a uniform sample and when from 0.2 to 2.5 grams of the substance are digested by the Kjeldahl-Gunning method, allowing four hours for the digestion, uniform results can be obtained for total nitrogen.

RECOMMENDATIONS.

The referee has concluded as a result of this work that the contention of W. D. Bigelow and F. C. Cook, that the present method for total nitrogen is

efficient, holds when care is taken that a well-mixed and uniform sample be used for analysis and that the oxidation be complete. To secure complete oxidation the cooperators choose generally a combined Kjeldahl-Gunning method. In this connection the referee wishes to call attention to the report of committee A on recommendations of referees for 1907. Under "(1) Nitrogen," recommendation 5, page 129, Bulletin 116, there is a recommendation that a special method be introduced combining the features of the two methods—the Kjeldahl and the Gunning. The referee finds no further action on this important point. He would therefore recommend—

(1) That on page 7, Bulletin 107, Revised, between "(b) Gunning method" and "(c) Kjeldahl method modified" there be inserted a Kjeldahl-Gunning method as follows:

(b) KJELDAHL-GUNNING METHOD.

Place the substance to be analyzed in a digestion flask, employing from 0.7 to 3.5 grams, according to its proportion of nitrogen. Add 0.7 gram of mercuric oxid, or its equivalent in metallic mercury, and from 20 to 30 cc of sulphuric acid. Start the digestion and, after frothing has ceased and contents of flask are no longer pasty, add from 7 to 10 grams powdered potassium sulphate. When digest is colorless cool and wash down the neck of the flask with water and continue the digestion till oxidation is complete. Finish as in the Kjeldahl method, omitting potassium permanganate.

(2) That in 7 (a), line 1, same reference, page 108, the words "or Kjeldahl-Gunning method" be inserted after "the Gunning method."

(3) That in the same bulletin, page 114, 7 (a) be made to read: "Employ the Kjeldahl-Gunning method, page 7, under 'I. Fertilizers.' Use from 0.2 to 2.0 grams of thoroughly mixed sample and digest for at least four hours."

(4) That the work for next year be a continuance of the separation of the nitrogenous bodies (meat proteins).

NOTES ON THE DETERMINATION AND VALUATION OF POTASH.

By P. F. TROWBRIDGE.

Many claims are being made on the part of certain fertilizer manufacturers as to the great advantage of manure concentrate or manure ashes, not only as to the plant food present, but as to the good effect upon the land due to the alkalinity of the material. The same manufacturers have difficulty in making the potash content of the fertilizer run uniform and requests are repeatedly received that the analysis of potash be modified to include total potash.

This can not be done according to the present fertilizer law of Missouri, which specifies that the potash must be soluble in water. In order to get some information at first hand the writer himself secured directly from the furnaces a sample of the ashes from burned manure and also a sample of ashes from a limekiln in the State. Examination of the alkalinity of these ashes shows that the manure ashes have an equivalent of 30.38 per cent of calcium oxid, while the wood ashes have an equivalent of 53.73 per cent.

Samples of these ashes were boiled for several hours with distilled water and thoroughly washed to separate the water-soluble potash as in the regular fertilizer analyses. The insoluble residue was then examined for total potash by the J. Lawrence Smith method to determine the amount of insoluble potash. The following tabulation shows the results obtained:

Potash content of manure and wood ashes.

Determinations.	Manure ashes.	Wood ashes.
	<i>Per cent.</i>	<i>Per cent.</i>
Soluble potash.....	5.916	4.670
Insoluble potash.....	7.702	.938
Total.....	13.618	5.608

It is quite probable that the large amount of dirt in the manure may have formed with the burned ashes an insoluble silicate, which would account for the large amount of insoluble potash.

An examination of five samples of ash from the leaves of the peach shows it to contain 26.588 per cent of soluble potash and 3.239 per cent of insoluble potash. The ash from several samples of timothy hay contains as high as 30 per cent soluble potash in the hay cut in the earlier stages of growth, while in the ash from the ripe hay the soluble potash is as low as 23 per cent. In these samples of ash from timothy hay only about 1 per cent of insoluble potash is found.

REPORT ON THE SEPARATION OF NITROGENOUS BODIES (MILK AND CHEESE).

By A. W. BOSWORTH, *Associate Referee*, and O. B. WINTER.

PLAN OF WORK.

As no recommendations were made for this line of work by the association last year, the referee has selected for study two of the newer methods which have been published recently. These methods are the Folin¹ method for the determination of ammonia and the Van Slyke² method for the determination of amino acid nitrogen.

It has been known³ for some time that the method of determining ammonia by distilling with magnesium oxid may give high results, and several attempts have been made to eliminate this source of error. The Folin method seems to be the best one of these, and has given good results when used by several workers.⁴

In applying the Folin method to cheese investigations it became necessary to determine what set of conditions would give the most accurate results and at the same time allow the ammonia-free extract to be used for the Van Slyke method.

The apparatus used for the ammonia determination was arranged in the manner described by Folin in his original article. Air was drawn through the apparatus by means of suction pumps, one pump for each determination. The water pressure was 42 pounds.

The cheese solutions were made by extracting 25 grams of cheese (which had been ground with sand) with 150 cc portions of water at 55° C. until

¹ Zts. physiol. Chem., 1902-3, 37:161.

² Ber. d. chem. Gesell., 1910, 43:3170.

³ Hart, Zts. physiol. Chem., 1901, 33:347.

⁴ Folin, Zts. physiol. Chem., 1902-3, 37:161; Kober, J. Amer. Chem. Soc., 1908, 30:1131; Gill and Grindley, J. Amer. Chem. Soc., 1909, 31:1249; Pennington and Greenlee, J. Amer. Chem. Soc., 1910, 32:561; Gebellen, Brymelsden and Haevardsholn, Chem. Ztg., 1909, 33:793; Denis, J. Biol. Chem., 1910, 8:427.

nearly 1,000 cc had been obtained. The volume was then made up to 1,000 cc and filtered.

For the determination of ammonia 100 cc of this solution, equal to 2.5 grams of cheese, were employed. As this is a much larger volume than is used by Folin a few determinations were run on a solution of ammonium chlorids of known strength in order to obtain some idea as to the amount of alkali and the length of time required to drive over all the ammonia.

It was found that 4 grams of sodium hydroxid or sodium carbonate and four hours of aeration would recover all the ammonia from 100 cc of ammonium chlorid solution containing 0.0280 gram of nitrogen.

In using sodium hydroxid, hydrolysis may take place, increasing the ammonia, or phosphates may be precipitated which contain ammonia and give low results. Hydrolysis may be prevented by the addition of sodium chlorid and the precipitation of the phosphates be prevented by the addition of potassium oxalate.¹

ANALYTICAL RESULTS.

These points were investigated with the results reported in the following tables. Some determinations were made by distilling with magnesium oxid, and these are also given.

Determination of ammonia in cheeses.

[Time of aeration, 4 hours.]

Sample.	Alkali used.	Nitrogen.
		<i>Gram.</i>
Cheddar:		
1.....	10 cc 40 per cent sodium hydroxid.....	0.0029
2.....	do.....	.0028
3.....	10 cc 40 per cent sodium hydroxid+5 grams sodium chlorid.....	.0032
4.....	do.....	.0028
5.....	4 grams sodium carbonate.....	.0027
6.....	do.....	.0028
	Magnesium oxid distilled:	
	First 150 cc.....	.0034
	Second 150 cc.....	.0006
	Third 150 cc.....	.0004
Camembert:		
1.....	10 cc 40 per cent sodium hydroxid.....	.0081
2.....	do.....	.0081
3.....	do.....	.0078
4.....	do.....	.0077
5.....	10 cc 40 per cent sodium hydroxid+10 grams potassium carbonate.....	.0076
6.....	do.....	.0078
7.....	4 grams sodium carbonate.....	.0077
8.....	do.....	.0078
9.....	4 grams sodium carbonate+10 grams potassium carbonate.....	.0077
10.....	do.....	.0079
11.....	do.....	.0076
12.....	do.....	.0081
13.....	Magnesium oxid distilled:	
	First 150 cc.....	.0085
	Second 150 cc.....	.0005
	Third 150 cc.....	.0003

The results obtained seem to indicate that the Folin method² can be used with great advantage for the determination of ammonia in cheese, and that the kind of alkali employed makes practically no difference. This is of great im-

¹ Folin, J. Biol. Chem., 1910, 8:497; Steel, *ibid.*, 1909, 7:365.

² After this paper was written one of the authors learned that Folin has improved his method. He now uses a small volume of sample (about 10 cc) and determines the ammonia caught in the acid by the colorimeter.

portance if we are to use the solution after it has been freed from ammonia for the determination of amino nitrogen by the Van Slyke method. Sodium hydroxid is to be preferred in this case, for the solution must be neutralized and evaporated somewhat and then brought up to the original volume (100 cc).

It is apparent at once that the Van Slyke method for amino nitrogen is applicable to cheese work. The only question arising is that of the particular value in this kind of work. It seems to the writers that the advantage in using the Van Slyke method lies in the fact that an indication as to the extent of the ripening of a cheese may be thus obtained.

This is shown in the following scheme, which was suggested in part by D. D. Van Slyke, the originator of the method.

SCHEME FOR THE PARTIAL ANALYSIS OF THE WATER EXTRACT OF CHEESE.

Make the water extract as usual, filtering through paper before using.

- (a) Determine total nitrogen in the extract.
- (b) Determine ammonia in the extract by the Folin method.
- (c) Determine amino nitrogen by the Van Slyke method, using a portion of the ammonia-free solution from (b) after it has been brought back to original volume.¹
- (d) Treat a portion of the original extract with an equal volume of concentrated hydrochloric acid and boil under a reflux condenser until completely hydrolyzed. Evaporate the solution to remove the hydrochloric acid and then make up to 100 cc and determine the ammonia by the Folin method.
- (e) Determine the amino nitrogen by the Van Slyke method in a portion of the ammonia-free solution from (d) after it has been brought back to original volume.¹

An analysis made according to this scheme will give:

- (1) Nitrogen as ammonia (b).
- (2) Amino nitrogen (c).
- (3) Amino nitrogen bound in peptid linking (e-c).
- (4) Nonamino nitrogen (a-[d+e]). This comes from the portion of the casein molecule containing arginin, histidin, prolin, oxyprolin, and tryptophan.

The ratio e:c indicates the average number of amino acids in the molecule of the peptids composing the mixture called the peptones and caseoses, i. e., it is a chemical index of the extent to which the protein in the extract is broken down. In a dipeptid the ratio is 2, in a tripeptid the ratio is 3, etc.

An analysis of a camembert cheese made according to this scheme gave the following results:

	Per cent.
Total soluble nitrogen.....	3.39
Nitrogen as ammonia.....	.43
Nitrogen as amino nitrogen.....	.25
Nitrogen as ammonia after hydrolysis.....	.76
Nitrogen as amino nitrogen after hydrolysis.....	1.80
Amino nitrogen bound in peptid linking.....	1.05
Nonamino nitrogen.....	.83

Ratio of e:c=1.80:0.25=7.2.

RECOMMENDATIONS.

It is recommended—

(1) That the Folin method for the determination of ammonia be further studied.

(2) That the Van Slyke method for the determination of amino acid nitrogen be further studied.

¹ This is done by adding a slight excess of acetic acid, evaporating to less than 100 cc, transferring to a 100 cc graduated flask and making up to volume.

REPORT OF COMMITTEE C ON RECOMMENDATIONS OF REFEREES.

By A. L. WINTON, *Chairman*.

(Food adulteration.)

SPICES.

It is recommended—

(1) That further study be made of the ether extract of paprika, particularly of the index of refraction, with a view to detecting added foreign oils.

Adopted.

(2) That samples of prepared mustard of known composition be submitted to collaborators for determination of crude fiber by the present official methods.

Adopted.

CONDIMENTS OTHER THAN SPICES.

It is recommended—

(1) That such of the methods given in the report of the associate referee as seem valuable in detecting spoilage be further studied. (See p. 118.)

Adopted.

COCOA AND COCOA PRODUCTS.

It is recommended—

(1) That methods for the determination of milk solids in milk chocolate be further studied.

Adopted.

DAIRY PRODUCTS.

It is recommended—

(1) That Paul's method of extracting fat from dairy products be further studied, and that the fat obtained by this method be studied as to its chemical and physical constants.

Adopted.

NITROGENOUS BODIES (MEAT PROTEINS).

It is recommended—

(1) That in Bulletin 107, Revised, page 108, 7 (a), there be added the following sentence: "If desired, 5 to 7 grams of potassium sulphate may be added in addition to the mercury of the Kjeldahl method."

Approved and referred to the association for final action in 1912.

(2) That the same modification of the Kjeldahl method be recognized as provisional for meat extracts, Bulletin 107, Revised, page 114, 7 (a).

Approved and referred to the association for final action in 1912.

(3) That the referee for next year make a further study of the separation of nitrogenous bodies (meat proteins).

Adopted.

WATER IN FOODS.

It is recommended—

(1) That the referee for next year make a comparison of the vacuum method (Bul. 122, p. 219) with the official methods for the determination of moisture in foods; and that he study other desiccating agents than sulphuric acid.

Adopted.

VINEGAR.

It is recommended—

(1) That the method quoted by the associate referee for glycerin (Ross, Bul. 137, pp. 61-63) be adopted as provisional.

Adopted.

(2) That the provisional method for pentosans (Bul. 107, Rev., p. 54) be applied to vinegar, with the direction for the use of the proper amount of hydrochloric acid to allow for the water in the vinegar.

Adopted.

(3) That the other methods proposed by the referee be continued for future study. (See p. 126.)

Adopted.

CEREALS.

It is recommended that the following action be taken in regard to the establishment of methods for the examination of wheat flour:

(1) That the method for the determination of moisture given in Bulletin 107, Revised, page 38 (1), be made official for wheat flour, and that a further study be made of the efficiency of the vacuum desiccator as compared with the vacuum oven.

Adopted; referred to association for final action in 1912.

(2) That Method B of the associate referee's report for the determination of ash be made a provisional method. (See p. 102.)

Adopted; referred to association for final action in 1912.

(3) That methods for the determination of the acidity of the water extract of flour be further studied with reference to the temperature of the water and time of extraction.

Adopted.

(4) That the method for the determination of the ether extract given in Bulletin 107, Revised, page 39, 5 (b) (1), be made official.

Approved and referred to the association for final action in 1912.

(5) That the method of Bryan, Given, and Straughn for the determination of soluble carbohydrates be given a more extended trial. (See statement of method below.)

Adopted.

(6) That protein be calculated from the nitrogen determined by the Kjeldahl or Gunning method, using the factor 5.70.

Adopted.

(7) That Winton's gasoline color value method be made provisional (Bul. 137, p. 144).

Adopted.

(8) That a study be made of methods for the determination of nitrites in flour.

Adopted.

(9) That experiments be made on the feasibility of determining acidity and nitrites in aliquots of the same water extract of flour.

Adopted.

The following statement of the method of Bryan, Given, and Straughn is submitted as showing the form in which it should be considered for adoption; details and discussion given in Circular 71:

BRYAN, GIVEN, STRAUGHN METHOD FOR THE DETERMINATION OF SOLUBLE CARBOHYDRATES.

(a) *Preparation of solution.*—Place 12 grams of the finely-ground material in a 300 cc graduated flask, with 1 to 3 grams of precipitated calcium carbonate to neutralize the acidity, add 150 cc of 50 per cent alcohol by volume (carefully neutralized), mix thoroughly, and boil on a steam bath for one hour, using a small funnel in the neck of the flask to condense the vapor. Cool, make to volume (300 cc) with 95 per cent alcohol (neutral in reaction), mix thoroughly, allow to settle. Transfer 200 cc to a beaker with a pipette, and

evaporate on a steam bath to a volume of from 20 to 30 cc, *but not to dryness*. This should remove all but traces of alcohol. Add 20 cc of water, stir, and transfer the solution to a 100 cc graduated flask, washing the beaker with water into the flask. Add to this enough saturated solution of neutral lead acetate from a burette or pipette to produce complete precipitation, but avoid an excess. Allow to stand 15 minutes and make up to a volume of 100 cc with water, shake well, and filter. At least 75 cc of filtrate should be obtained. Add anhydrous sodium carbonate or potassium or sodium oxalate to precipitate all the lead, allow to stand 15 minutes, and pour onto an ashless filter. Test the filtrate for lead with small quantities of the precipitating agents mentioned above and refilter if necessary. This solution represents the sugars from 8 grams of the original material and is used in the following determination.

(b) *Reducing sugars*.—Use 25 cc of the filtrate together with 25 cc of water as the sugar solution for Munson and Walker's method (Bul. 107, Rev., p. 241), or 25 cc of the solution for Allihn's method (*ibid.*, p. 49). With Allihn's method the amount of dextrose found is multiplied by the factor 1.044 to obtain the equivalent in invert sugar.

(c) *Sucrose*.—Place 50 cc of the filtrate from (a) in a covered 400 cc beaker. In case sodium carbonate was used to throw out the lead, add a small piece of litmus paper and neutralize with acetic acid, then add 5 cc of concentrated hydrochloric acid, and allow to stand overnight for inversion. If potassium or sodium oxalate was used for removing lead it is not necessary to neutralize, but the acid can be used direct. At the expiration of 24 hours neutralize with anhydrous sodium carbonate, wash into a 100 cc flask, and make up to the mark. Filter, if necessary, and use 50 cc for the determination of total sugars as invert by the method of Munson and Walker or 25 cc by the method of Allihn. Subtract the percentage of reducing sugars before inversion calculated as invert sugar from the percentage of total invert sugar after inversion and multiply this product by 0.95 to obtain the percentage of sucrose.

For more exact results it is necessary to determine the volume occupied by the 12 grams of material used in this work and to account for it. A large number of determinations has shown the average volume of 12 grams to be 9 cc. Therefore the correction would be 0.97, and, hence, the percentages of original sugars and sucrose should be multiplied by this factor to obtain the most accurate results.

FLAVORING EXTRACTS.

It is recommended—

(1) That the method of determining vanillin, coumarin, normal lead number, and residual color in one weighed portion, as proposed by Winton, Lott, and Berry, be provisionally adopted, changing the text of the method as adopted at the last meeting (Bul. 137, p. 68) so as to include the detail of precipitation at a standard temperature, 37° to 40° C. (Bul. 137, p. 120), and to make quantitative the provisional method for the determination of color in the filtrate, as given in Bulletin 107, Revised, p. 159, 11 (b). (See p. 144.)

Adopted.

(2) That the preceding method for determining vanillin, coumarin, normal lead number, and residual color in filtrate in one weighed portion of sample be further studied next year for the special purpose of ascertaining the limits of composition of standard vanilla extracts.

Adopted.

(3) That Tolman's method for determining per cent of color insoluble in amyl alcohol (Marsh reagent) be adopted as provisional, and that the text of the method as published in the Proceedings of the Association of Official Agricultural Chemists (Bul. 132, p. 90) be inserted as (c) under "11. Test for coloring matter," in Bulletin 107, Revised, page 159. Twenty-five cubic centimeters of the sample is sufficient for the test. It is further recommended that this method be studied next year for the purpose of determining the range of values for pure vanilla extracts.

Adopted.

(4) That the provisional and other methods for the determination of benzaldehyde in almond extract be further studied, with the view to determining

the reliability of the methods and also the conditions under which aldehyde is oxidized to benzoic acid in commercial extracts, as well as the extent of such oxidation. (Bul. 137, p. 74; Cir. 66, p. 21.)

Adopted.

(5) That Mitchell's modification of the Seeker test for ginger be further studied. (See p. 137.)

Adopted.

(6) That the method for the detection of capsicum in ginger extract, as proposed by Doyle, modifying the La Wall method, be adopted as provisional. The Doyle method is not essentially different from La Wall's. The details of procedure, however, are such as to make the test more positive and are set forth more clearly than in the latter method. (See p. 137.)

Approved and referred to the association for final action in 1912.

(7) That the Street-Morrison method (Bul. 137, p. 76) and other available methods for examining and identifying the components of the total solids of ginger extracts be a subject for study next year. Such a method is necessary for proving adulteration in alcoholic extracts of ginger.

Adopted.

(8) That the subject of the determination of oil of nutmeg in nutmeg extract be studied further and that other methods be tried next year, as both of the methods tried this year proved utterly unreliable.

Adopted.

(9) That for the determination of oil of wintergreen in wintergreen extracts both of the following methods be further studied:

First. Howard's method as described in J. Ind. Eng. Chem., 1911, 3:252, using cold dilute sulphuric acid (1:2) for the floating medium.

Second. Hortvet and West's method of saponifying the oil and weighing as salicylic acid. (J. Ind. Eng. Chem., 1909, 1:90.)

Adopted.

(10) That the Howard method (Bul. 137, p. 76) for the determination of oil of peppermint in alcoholic solutions, which was adopted provisionally last year, be given further study. This method has been modified, in the interests of greater accuracy, by its author, and the new method is found in J. Ind. Eng. Chem., 1911, 3:252.

FATS AND OILS.

It is recommended—

(1) That further work be done on the Emery method next year. (U. S. Dept. Agr., Bureau of Animal Industry, Cir. 132.)

Adopted.

(2) That the provisional method for the preparation of samples be made official. (Bul. 107, Rev., p. 129.)

Approved for final action in 1912.

(3) That the referee for next year study the advisability of changing the official method for the determination of specific gravity at 100° to a similar method at 75° C.

Adopted.

(4) That method "(c) Zeiss Butyro Refractometer" (Bul. 107, Rev., p. 132) be made official instead of provisional, as at present.

Approved for final action in 1912.

(5) That the provisional method for the melting point of fatty acids (Bul. 107, Rev., p. 135 (b)) be made to include the fat as well as the fatty acids and to read as follows:

Draw the melted fat or fatty acids into a thin-walled capillary tube, 1 inch or 2 inches long, according to the length of the bulb of the thermometer used. Seal one end of the tube and allow the fatty acids to cool on ice from 12 to

15 hours. Attach to the bulb of a delicate thermometer graduated to 0.2° , immerse in a large test tube of water surrounded by a beaker of water, and heat very slowly. An apparatus similar to that indicated for use in the Wiley method, but smaller, will prove satisfactory. The point at which the substance becomes transparent should be taken as the melting point.

Adopted, final action.

(6) That method "12. Determination of free fatty acids" (Bul. 107, Rev., p. 143) be made official instead of provisional, as at present.

Approved for final action in 1912.

(7) That the Halphen reaction for cottonseed oil (Bul. 107, Rev., p. 144, 17(b)) be made official instead of provisional.

Approved for final action in 1912.

(8) That the Bechi or silver nitrate test for cottonseed oil (Bul. 107, Rev., p. 145, 17(c)) be made official.

Approved for final action in 1912.

(9) That the Baudouin test for sesame oil (Bul. 107, Rev., p. 146, 17(e)) be made official.

Approved for final action in 1912.

(10) That the Villavecchia test for sesame oil (Bul. 107, Rev., p. 146, 17(f)) also be made official.

Approved for final action in 1912.

(11) That any cut appearing in the text of the chapter on fats and oils. Bulletin 107, Revised, be considered merely as an illustration and not as an integral part of the method.

Approved for final action in 1912.

A supplementary report on the separation of nitrogenous bodies (milk and cheese) was made by Mr. Street as chairman of committee A (see page 86).

A NOTE ON THE DETERMINATION OF BENZALDEHYDE IN LIQUEURS, DISTILLED LIQUORS, AND CORDIALS.

By F. G. SMITH.¹

The method used consisted of a simple distillation and a precipitation with phenylhydrazin as proposed by Denner² and further improved by Denis and Dunbar.³ Folin and several other investigators claim that many fruit products show about 0.015 per cent benzoic acid by the quantitative methods now in use. This fact makes the oxidation method for the determination of benzaldehyde unreliable for traces. Work done recently on maraschino liqueurs and cherries shows practically no benzaldehyde in genuine maraschino preparations. This would be expected from the fact that maraschino is prepared from a cherry mash and sometimes the distillate is flavored with broken cherry pits. Several artificial maraschino liqueurs were prepared containing a known amount of commercial benzaldehyde, which was assayed by the Denis-Dunbar method and found to contain 87 per cent of this substance. A fractional distillation of the first maraschino liqueur prepared gave about 98 per cent of the benzaldehyde recovered in the first two 10 cc fractions; the next 20 cc fraction recovered the remainder. The total recovery from the 200 cc distilled was about 90 per cent of the benzaldehyde present. This liqueur stood in contact with the air some time after being prepared, and some of the benzaldehyde was undoubtedly lost.

¹ Presented by Mr. A. S. Mitchell.

² Zts. anal. Chem., 1890, 29: 228.

³ J. Ind. Eng. Chem., 1909, 1: 256.

Several fractional distillations of an artificial maraschino gave the following amounts of benzaldehyde:

Recovery of benzaldehyde by fractional distillation of three 200 cc samples of artificial maraschino.

Number of distillations.	Fraction.	0.10 gram commercial benzaldehyde present.		0.06 gram commercial benzaldehyde present.
		Sample 1: Distilled in current of carbon dioxide.	Sample 2: Distilled in air.	Sample 3: 50 grams powdered sodium chlorid added; distilled in air.
	Cc.	Gram.	Gram.	Gram.
1.....	10	0.0600	1.0551	0.0468
2.....	10	.0184	.0193	.0062
3.....	20	.0070	.0105	.0012
4.....	20	.0019	.0016	.0019
5.....	20	.0005	.0000
6.....	20	.0023	.0011
7.....	20	.0004	.0008
8.....	20	.0000	.0000
Total amount.....		.0905	.0884	.0591
Per cent recovered.....		90.5	88.4	93.5

The high per cent of benzaldehyde recovered in the sodium chlorid distillation is due to a probable decomposition of sucrose resulting in volatile substances precipitable by phenylhydrazin. Distillations of maraschino liqueurs prepared with sucrose showed an increased precipitate in the latter fractions, while those prepared entirely of invert sugar, as in the case of No. 2, show no such increase in the last three fractions.

The conditions essential to a complete precipitation by phenylhydrazin were studied on pure solutions of benzaldehyde and on artificial liqueurs prepared in this laboratory as well as on a number of genuine and imitation maraschinos. In this work the volume from which the benzaldehyde was precipitated was kept as small as possible, as a large volume of water seems to increase the decomposition of phenylhydrazin, caused by the action of the light and air.

Alcohol up to 20 per cent by volume in the solution did not affect the determination, as will be shown by the following table, which also shows that an excess of alcohol can be boiled off without affecting the result. This is true of quite large excesses of the reagent, but the precipitate is more difficult to handle.

Benzaldehyde determinations in the presence of varying amounts of alcohol.

[0.10 gram present.]

Number.	Benzaldehyde found.	Alcohol.	Denis and Dunbar No. 2 reagent.
	Gram.	Per cent by volume.	Cc.
1	0.0872	5	5
2	.0883	10	5
3	.0882	20	5
4	.0817	50	5
5	.0882	1 10	5
6	.0886	1 20	5
7	.0876	2 10	5
8	.0877	2 20	5
9	.0868	4	2
10	.0886	4	5
11	.0882	4	10
12	.0882	4	15

¹ Alcohol boiled out. ² Added after boiling out.

The solubility of a pure benzalphenylhydrazone in distilled water was found to be less than 3 parts in 100,000 and is not appreciably increased by a small per cent of alcohol. The 12 determinations on a 0.10-gram sample of the commercial product used gave in each case within 0.5 mg of 0.088 gram of benzaldehyde.

The method used for weighing the precipitated benzalphenylhydrazone was found to give admirable results. It consisted in balancing two 9-cm filter papers, filtering through the two papers superimposed, and counterbalancing the one against the other in weighing the precipitate. The precipitates were dried in a 60° air oven and overnight in a sulphuric acid desiccator. Four determinations were made on the benzaldehyde used, with the following results:

Commercial benzaldehyde.	Benzaldehyde recovered.
0.1-----	0.0883
.01-----	.0078
.001-----	.0009
.0001-----	slight but distinct precipitate.

One milligram of benzaldehyde was added to 100 cc of distilled water and distilled in a current of carbon dioxid. Practically all of the benzaldehyde was recovered.

The factor for the conversion of benzalphenylhydrazone into benzaldehyde is 0.5408, and for benzal-semicarbazid to benzaldehyde 0.7213.

Although distillation in air seems usually to recover the full amount of the benzaldehyde, a distillation in carbon dioxid always does, and for this reason is to be preferred. It was found helpful to wash the precipitate once in each case with dilute acetic acid.

Several samples of imported maraschino cherries, probably genuine, and two imported maraschino liqueurs were found to contain the following amounts of benzaldehyde:

	Grams per 100 cc.
Maraschino liqueur-----	¹ 0.0018
Do-----	.0000
Maraschino cherries, juice-----	.0001
Do-----	.0000
Do-----	.0003
Do-----	.0000
Imitation products:	
Maraschino liqueur-----	.0150
Maraschino cherries, juice-----	.0065
Do-----	.0177
Do-----	.0062
Do-----	.0000
Do-----	.0160
Do-----	.0120
Do-----	.0035
Do-----	.0100
Do-----	.0232
Do-----	.0333

The benzalphenylhydrazone in each case is identified by the melting point and by the Melzer test (see page 195), which gives positive results with 1 mg of benzaldehyde or directly with 2 or 3 mg of the benzalphenylhydrazone. In

¹The melting point of this precipitate was very low, indicating that it was not benzalphenylhydrazone, but a sugar decomposition product.

all cases the precipitate was found to be quite pure benzalphenylhydrazone if appreciable in amount.

The precipitation of benzaldehyde by semicarbazid hydrochlorid as benzal semicarbazone was found to give very concordant results and to agree very closely with the phenylhydrazone method.

Benzaldehyde recovered from 0.10 gram commercial product.

Precipitated in 20 per cent alcohol.....	0.0888
Precipitated in 50 per cent alcohol.....	.0436
0.01 gram commercial.....	.0078
0.001 gram commercial. No precipitate.	
Alcohol boiled out.....	.0888
Ammonia added.....	.0916
Acetic acid added.....	.0892

When using the semicarbazid method the precipitate should be allowed to stand overnight, as it does not form as readily as the phenylhydrazone. The semicarbazone formed is not contaminated with decomposition products as in the case of the hydrazone and it is much easier to handle. The phenylhydrazin, however, is much more delicate in detecting traces, as the semicarbazid hydrochlorid gives no precipitate with amounts up to 2 or 3 mg. The phenylsemicarbazid hydrochlorid was dissolved in water to make a 1 per cent solution. This reagent is fairly stable while the phenylhydrazin must be frequently redistilled and always prepared absolutely fresh.

*Melzer method for the detection of benzaldehyde and phenol.*¹—Add to 1 cc of phenol solution, as an aqueous distillate, 2 cc concentrated sulphuric acid, and 1 to 2 drops of benzaldehyde and boil. To test for benzaldehyde, add phenol. The initial yellowish brown color becomes dark red and a red resinous substance separates out on dilution. Let cool and add 10 cc of water and 20 per cent potassium hydroxid until distinctly alkaline. Phenol, in the presence of benzaldehyde, gives a blue violet color. The resultant dye can be extracted from the acidified solution with ether. The method is sensitive to 0.005 gram of phenol.

NOTE ON A TENTATIVE METHOD FOR THE DETERMINATION OF ESSENTIAL OIL IN ALCOHOLIC SOLUTIONS.

By R. S. HILTNER.

Owing to the apparent failure of existing methods for the determination of oil of peppermint and of nutmeg in the so-called extracts the associate referee has attempted to devise a new method that will give more satisfactory results. He offers the following only tentatively as an outline of a process that seems promising:

Prepare a quantity of hydrocarbon oil (boiling at 175° to 200° C.), by fractional distillation of commercial kerosene, pipette 10 cc of the extract sample into a Babcock milk bottle, add 1 cc (accurately measured) of hydrocarbon oil, 2 drops of concentrated hydrochloric acid, and 25 cc of hot water; shake vigorously, warm on the steam bath to about 80°, whirl in a centrifuge, add water so as to bring the floating oil into the neck of the flask, and again whirl. Determine the refractive index of the separated oil and of the hydrocarbon oil used at 20° C. To ascertain the quality of the oil present in the sample it may

¹ Zts. anal. Chem., 1898, 37: 345.

be necessary to float on water the essential oil in another portion, and determine its refractive index, following in a general way the procedure for determining lemon oil as given in Bulletin 107, Revised, page 156, paragraph 4 (a). It appears possible to calculate the percentage of essential oil from these data.

Mr. Winton called attention to the fact that it was very necessary that the methods used by the Government chemists in work done under the food law in determining nitrites in flour should have the approval of the association and be given the standing of official methods. To this end it was moved that permission be given to insert these methods in the Proceedings of 1911 at the close of the report of the referee on cereals, in order that they might be before the association with a view to their adoption at the next meeting.

The motion was carried. (See p. 113 for statement of methods.)

THIRD DAY.

WEDNESDAY—MORNING SESSION.

The Secretary of Agriculture addressed the association at the opening of the session, calling attention especially to the varied activities of the Department of Agriculture, the many problems waiting solution, and the fundamental part played in nearly all of the work by the chemists. Good and cheap food, reliable fertilizers and insecticides, good roads, and cold storage in its bearing on both supply and quality were among the topics discussed. The Secretary in closing expressed his desire to facilitate the work of the association in every way possible, with the cooperation of Dr. Wiley as secretary of the association.

Mr. Withers, as chairman of the committee on a journal of agricultural research, reported that Congress had been asked to appropriate \$20,000 for the publication, in the form of a journal, of the original and technical work of the experiment stations. The resolution adopted by the association at its last meeting indorsing this recommendation was duly transmitted by the committee as requested. The item in the appropriation bill was thrown out by the House upon a point of order, and later inserted by the Senate, but was finally stricken out in conference.

As it appeared to the committee impracticable to take further action at this time they requested to be discharged.

The report was accepted and the committee discharged as recommended.

REPORT ON FEEDS AND FEEDING STUFFS.

By G. M. MACNIDER, *Referee*.

ACIDITY OF FEEDS.

The work on the determination of the acidity of feeds has not been pushed this year, as the determination of acidity is of little consequence in estimating the value of a feed except in the case of gluten feeds and feeds which may spoil by fermentation, etc. In such cases the estimation of the water-soluble acidity gives the desired information in regard to the feed. For the determination of the total soluble acidity the method proposed in the last report affords a rapid

and accurate means of estimating the acidity of a feed. The method is as follows:

Weigh 10 grams of the sample into a shaking bottle, add 200 cc distilled water, and shake for 15 minutes. Filter the extract through a folded filter and take an aliquot of 20 cc (equal to 1 gram of sample) for the titration. Dilute with 50 cc distilled water and titrate with standard decinormal sodium hydroxid solution, using phenolphthalein as indicator.

The recommendation of the committee "that the subject of the acidity of commercial feeds be studied with special reference to eliminating the error due to the proteins" has not been taken up. To determine satisfactorily the effect of the acidity of the proteins would require a thorough investigation into the reactions of the different proteins occurring in the various feeds, and it was not thought advisable to take up such a piece of research with this problem.

As gluten feeds usually show a higher acidity than other feeds and are among the few which are treated chemically during the process of manufacture, the nature of their acidity has received considerable attention by a number of stations. The references to this literature are given in the last report. Jordan¹ has recently published the results of investigations on the "acidity of gluten feeds." In this work the nature of the acidity of the feeds and also of the steep water, which is added to the feed during the process of manufacture, was studied. The author concludes that the acidity of gluten feeds is caused by the addition of steep water, a by-product obtained in the manufacture of corn products. The steep water contains two constituents which give it an acid reaction, namely, amino acids and phosphorus compounds. The steep water contains traces of mineral acids. They are present in such small quantities that they need not be considered as imparting any deleterious properties to the feed when steep water is added to it. This work bears out the statements which have previously been made in regard to the acidity of gluten feed; i. e., that the acidity is not caused by the presence of mineral acids; and it is, therefore, misleading to report the acidity of a feed in terms of a mineral acid.

COMPARISON OF THE OFFICIAL (ETHYL ETHER) METHOD FOR DETERMINING FAT WITH THE PETROLEUM ETHER METHOD.

The petroleum ether method for determining fat in cottonseed products was compared with the official method, as recommended, to ascertain the difference in the results by the two methods. The petroleum ether method, which has been adopted by the Cottonseed Crushers Association for determining oil in cottonseed products, is as follows: Extract 2 to 5 grams of the meal, without previous drying, for three hours in a Soxhlet apparatus with petroleum ether boiling under 65° C. Then evaporate off the ether, weigh the residue, and report as oil.

¹ New York (Geneva) Agr. Exper. Sta., Tech. Bul. No. 16.

ANALYTICAL DATA.

The following comparative work has been done:

Cooperative work on fat in cottonseed meal by two methods.

Number and analyst.	Official ethyl ether method.	Petroleum ether method.	Number and analyst.	Official ethyl ether method.	Petroleum ether method.
F. D. Fuller, Indiana: ¹	<i>Per cent.</i>	<i>Per cent.</i>	G. M. MacNider, North Carolina—Continued.	<i>Per cent.</i>	<i>Per cent.</i>
08.....	8.31	8.02	4294.....	7.47	7.12
09.....	9.18	9.13	4296.....	8.16	7.93
010.....	6.55	5.85	4297.....	7.35	7.20
011.....	8.38	8.21	G. L. Bidwell and C. E. Goodrich, Washington, D. C.: ¹		
012.....	8.92	8.54	A.....	7.39	7.51
013.....	7.84	7.81	B.....	8.12	7.90
014.....	8.24	7.87	C.....	5.63	5.62
015.....	7.83	7.25	D.....	4.71	4.80
016.....	8.60	8.30	E ²	10.69	10.22
017.....	7.59	7.26	J. B. Herron, Texas:		
018.....	7.14	6.79	1.....	7.58	7.18
019.....	8.31	8.34	2.....	8.73	8.60
020.....	12.52	12.53	3.....	6.78	6.54
021.....	7.71	7.79	4.....	8.18	8.03
022.....	8.32	8.34	5.....	6.10	5.80
023.....	7.78	7.25	6.....	8.56	8.26
024.....	9.02	8.46	7.....	6.69	6.86
025.....	8.08	7.64	8.....	7.75	7.60
026.....	4.57	4.53	9.....	7.85	7.91
G. M. MacNider, North Carolina:			10.....	8.63	8.63
4290.....	7.72	7.30			
4291.....	9.54	9.17			
4292.....	8.10	7.73			

¹ Results are averages of two or more determinations.

² Cold-press meal.

The average difference in the results is 0.29 per cent in favor of the ethyl ether; the greatest difference is 0.70 per cent, the smallest 0.01 per cent. With eight determinations the petroleum ether gives slightly higher results than the ethyl ether.

COMMENTS BY ANALYSTS.

F. D. Fuller: The results obtained, with few exceptions, show what might be expected, namely, that petroleum ether boiling under 65° C. removes less fat than does ethyl ether. Inasmuch as ethyl ether dissolves chlorophyll, resins, gums, alkaloids, and similar bodies in respect to which petroleum ether is almost inert it appears that the extract obtained by using petroleum ether more nearly represents the amount of true fat than is the case when ethyl ether is used as the solvent, although lack of time prevented a comparative study of the fat constants.

The advantages of using petroleum ether are obvious—first, the extraction is made without previous removal of moisture; second, the extraction is completed in three hours; third, the petroleum ether can be obtained for approximately 30 cents a gallon, an item which naturally appeals to the commercial chemist; and fourth, the extract undoubtedly more nearly represents the pure fat content of the substance under examination.

The chief disadvantages in using petroleum ether are that at least two hours are required to obtain an extract whose weight is constant, and that petroleum ether does not remove certain substances soluble in ethyl ether which heretofore have been counted as fat and in many cases considered as such in experiments in animal nutrition.

G. M. MacNider: The advantages of the petroleum ether method for the commercial chemist are very great—first, the cost of the petroleum ether is very much less than ethyl ether; second, the sample does not have to be dried before extraction, and the time required for extraction is three hours against sixteen hours by the official record.

G. L. Bidwell: I do not like to see the petroleum-ether method made official and used in all cases on cottonseed meals. In some samples it runs higher, and in others lower than the official method. I believe that it does have value as a control method in the mills, but think the variations from the official method are too great.

From these data it is seen that the average difference in the results by the two methods is 0.29 per cent in favor of the ethyl ether. From other work which has been done this average seems to represent the difference which may usually be expected between the two methods. It is known that the extract by petroleum ether represents more nearly the actual fat than the ethyl ether extract. Petroleum ether is very nearly inert in regard to chlorophyl and other vegetable compounds which are readily soluble in ethyl ether. The saving to the commercial chemist when the petroleum-ether method is used in both the cost of the solvent and the time required to make the analysis is very large, and it therefore seems advisable for the association to recognize this method.

COMPARISON OF THE PROPOSED MODIFICATION OF THE METHOD FOR THE DETERMINATION OF CRUDE FIBER WITH THE OFFICIAL METHOD.

In compliance with the recommendation of the committee, the proposed modification of the official method for the determination of crude fiber was studied. The method is as follows:

Place 2 grams of the sample in a wide-mouth Erlenmeyer flask of liter size, inserting a small air condenser in the mouth of the flask to prevent concentration, due to the loss of steam. To the sample add 200 cc of a 1.25 per cent solution of boiling sulphuric acid, as in the official method. Heat to boiling, and after boiling for thirty minutes treat as follows: Neutralize with a 10 per cent solution of sodium hydroxid, using a few drops of phenolphthalein as indicator, approximately 25 cc of sodium hydroxid are required. Add at once 200 cc of a 2.656 per cent solution of boiling sodium hydroxid and continue the digestion at the boiling point for thirty minutes longer, in the same manner as in the treatment with acid. Then filter the alkaline solution containing the fiber residue through a linen cloth rapidly and wash repeatedly with boiling water. Transfer the fiber residue to a tared platinum Gooch crucible and wash with alcohol and ether. Dry at 100° C. and weigh. Ignite the dried residue and again weigh, the loss in weight giving the weight of fiber.

ANALYTICAL RESULTS.

The following comparative work has been done:

Comparison of the proposed modified method with the official method for determining crude fiber.

Number of sample and analyst.	Sample.	Official method.	Proposed method.
N. H. Ulman, Pennsylvania: ^{1 2}			
5272.....	Blatchford's calf meal.....	6.61	8.02
5274.....	Blue ribbon dairy feed.....	10.48	12.80
5278.....	Cottonseed feed.....	28.35	31.22
5343.....	Alfalfa meal.....	28.35	30.00
5351.....	Cottonseed meal.....	9.52	13.78
5378.....	Gluten feed.....	6.55	8.10
E. C. Gildroy, Pennsylvania: ^{1 2}			
5272.....	Blatchford's calf meal.....	6.61	6.76
5274.....	Blue ribbon dairy feed.....	10.48	11.48
5278.....	Cottonseed feed.....	28.35	31.32
5343.....	Alfalfa meal.....	28.35	28.04
5351.....	Cottonseed meal.....	9.52	11.07
5378.....	Gluten feed.....	6.55	7.85
H. Hill, North Carolina:			
3954.....	Cottonseed feed.....	22.15	22.85
3956.....	Corn chops.....	8.10	8.59
3984.....	Wheat bran.....	9.18	9.32
3902.....	Scocoates.....	9.59	9.88
3933.....	Middlings.....	1.37	1.45
3940.....	Shipstuffs.....	6.35	6.26
G. L. Bidwell and C. E. Goodrich, Washington, D. C.: ¹			
C.....	Cottonseed feed.....	22.33	21.39
D.....	do.....	20.87	20.57
E.....	Cold press meal.....	24.18	24.50
G.....	Corn product.....	8.23	8.56
H.....	Wheat bran.....	9.67	11.25
I.....	do.....	11.15	11.46
J.....	Hen feed.....	3.42	3.75
K.....	Gluten feed.....	7.86	8.53
L.....	Feed meal.....	6.13	6.64

¹ Results are averages of two or more determinations.

² Reported by James W. Kellogg.

James W. Kellogg: It takes from two to seven hours to filter the residue through the Gooch crucibles after the final washing of the residues has been accomplished. It took about two hours to filter the samples through the linen cloths, which possibly might have been due to the fact that they became very mucilaginous after boiling in the presence of both the acid and the alkali. This condition was undoubtedly the cause of the slow filtrations through the Gooch crucibles. The determination for crude fiber on these samples by the official method occupies less than two hours for the boiling and filtration through the gooch. The proposed method is very unsatisfactory and an unreliable method to use.

H. Hill: The large amount of solution present with the alkali digestion is very inconvenient, causing slow boiling and excessive bumping. There is uncertainty about reaching the exact neutral point when neutralizing cottonseed feeds with the 2.656 per cent sodium hydroxid solution, due to the red color of the acid solution. Filtration through the linen was slow and through the gooch very slow. More time was required to make 6 determinations by the new method than is required to make 12 determinations by the official method. The method is expensive, more sodium hydroxid is required, and considerable alcohol and ether are wasted with each determination. The new method is more inconvenient, consumes more time, and gives higher results than the official method.

G. L. Bidwell: The proposed crude fiber method is not satisfactory. There is no great gain in using it, and the results are not strictly comparable with those given by the official method.

These results cover quite a wide range of feeds and would appear to constitute a fair trial. As will be seen from the table, the results by the proposed method are, in all but four cases, higher than the results by the official method. The greatest difference between the results by the two methods is 4.26 per cent, the smallest 0.08 per cent. In many of the determinations the results by the proposed method are higher than those by the official method by 1 per cent and more.

The results obtained by the two Pennsylvania chemists, working separately on the same samples, show a wide variation, while each chemist was able to obtain satisfactory checks on his own work, and, as these chemists found no difficulty in checking each other's work by the official method, this indicates that it is difficult to obtain satisfactory results by the proposed procedure. The plan of treating the samples with alcohol and ether after the digestions are made is not a good one, as with feeds high in fat the fat will unquestionably reduce the solvent action of the acid and alkali on the sample. It is seen, therefore, that the proposed method gives higher results than the present official method, requires more time, and is more difficult to operate.

RECOMMENDATIONS.

It is recommended—

(1) That the method suggested for determining the acidity of feeds be provisionally adopted. (See p. 198.)

Also that in reporting the acidity of feeds the results be stated in terms of cubic centimeters of the sodium hydroxid used or its equivalent in grams of sodium hydroxid.

(2) That the association recognize the petroleum ether method for determining fat in cottonseed products.

(3) That the proposed modification of the official method for the determination of crude fiber be no further considered.

(4) (On account of lack of time neither the referee nor the associate referee has been able to take up the study of the protein factor and therefore the following recommendation should be carried over to another year.)

That the referee make a study of the literature on the amount of protein in the various vegetable products used for feed, and report to the association at the 1912 meeting on the advisability of adopting more accurate factors for converting nitrogen into protein than the present factor of 6.25.

REPORT ON SUGAR AND MOLASSES.

By WILLIAM E. CROSS, *Referee.*

Owing to the late date of my taking up the work as referee (May) it was thought advisable to confine the investigations almost entirely to the recommendations of last year. Two samples only were sent out, the previous year's experience having shown the difficulty of securing cooperation when too much work was given. The samples consisted of (1) No. 16, a raw Cuban sugar, and (2) No. 18, a centrifugal molasses.

The following instructions accompanied the samples sent to the various co-operators:

INSTRUCTIONS FOR COOPERATIVE WORK.

MOISTURE—(MOLASSES).

Sample A.

Method 1. Determine moisture in 2 grams of sample by heating 10 hours at 100° C. with sand, according to method 3, page 65, Bulletin 107, Revised.

Method 1a. Determine moisture by heating 2 grams of sample for 10 hours at 100° C. without sand.

Method 2. Determine moisture in 2 grams of sample by heating on 6 grams of sand in vacuum at 70° C. Note number of hours required to obtain constant weight.

Method 3. Determine moisture in 2 grams of sample by following method: Weigh out into dish containing 50 grams of sand (free from iron). Warm in an oven, then add a little distilled water and mix thoroughly. Dry at 70° C. for 2 hours in a steam oven and thereafter, till weight is constant, in vacuo. Weight judged constant when 2 hours' further warming gives less than 0.1 per cent decrease.¹

Method 3a. Repeat 3, but heat in vacuum at 100–105° C., instead of 70° C.¹

Method 4. Determine moisture by Brix spindle. (See areometric method (1), p. 65, Bul. 107, Rev.)

Method 5. Refractometer. Make refractive index reading and convert to percentage moisture by means of Gearlign's tables:

(a) In a concentrated form.

(b) Half diluted with water.

(c) Half diluted with a saturated solution of sugar, using formula—

$$X = \frac{(A+B) C - BD}{A}$$

A=weight of material taken and mixed with B.

B=weight of sugar solution.

C=per cent dry substance of above mixture, obtained from refractive index.

D=per cent dry substance of pure sugar solution obtained from refractive reading.

MOISTURE—(SUGAR).

Sample B.

1. Determine moisture by official method, page 64, Bulletin 107, Revised.

2. Determine moisture by refractometric determination of solution of sugar in own weight of water.

¹ Modification of German official method.

POLARIZATION (SUGAR AND MOLASSES).

1. Weigh out normal weight, clarify (lead subacetate solution), make up to 100 cc (or more if necessary for accurate polarization), and polarize (according to Method c, Bul. 107, Rev., p. 40), single and Clerget.

2. Weigh out normal weight, make up to volume required, clarify with Horne's dry lead subacetate (J. Amer. Chem. Soc., 1904, 26:186) and polarize, single and Clerget.

3. (Molasses only.) Weigh out normal weight, add lead subacetate solution, make up to 200 cc, filter; to 50 cc of filtrate add 1 cc of 30 per cent acetic acid and 2 cc of alumina cream, make up to 55, filter, and measure, single polarization.

3a. Repeat 3, using Horne's dry lead instead of subacetate solution. (Record all dilutions and polarization readings, single and invert, and temperatures.)

It is important that work on samples should be commenced as soon as possible after their receipt on account of fermentation changes which are liable to occur. * * *

RESULTS OBTAINED.

MOISTURE CONTENT OF MOLASSES.

The main object of the work prescribed on moisture methods was to continue the study of the application of the refractometric method to those molasses, etc., which are too dark to be read directly. It was also intended to secure additional data on the comparison between the provisionally prescribed method of drying at atmospheric pressure with the vacuum drying prescribed for substances containing much levulose, etc., and with the drying method officially prescribed in Germany. Owing probably to the awkwardness of the vacuum determinations, however, very little cooperation along these lines was secured.

The following table shows the results obtained on moisture methods:

TABLE 1.—Comparative percentage results on the determination of moisture in molasses.

Name.	Heating 10 hours at 100° C. with sand.	Heating 10 hours at 100° C. without sand.	Vacuum at 70° C.	Hours.	Vacuum at 70° C., 50 grams sand.	Hours.	Brix.	Refractometer.		
								Undiluted.	Diluted with water.	Diluted with sugar solution.
A. Given, Washington, D. C.	21.37	21.26	21.10	25	22.3	26	16.76	20.25	19.04	18.10
W. E. Cross, New Orleans, La.	20.42	20.45	17.20	20.73	19.24	20.23
S. F. Sherwood, Washington, D. C.	21.96	21.25	20.15	26	20.70	26	16.50	20.35	19.72	20.64
W. D. Horne, New York, N. Y.	22.15	20.81	19.43	18.36
W. G. Taggart, New Orleans, La.	21.21	20.32	17.24	20.50
H. Z. E. Perkins, New Orleans, La.	21.55	20.18
R. S. Hiltner, Denver, Colo.	21.96	21.40	20.80	20	20.70	20	17.80	20.70	20.10	21.00
G. H. Hardin, New York, N. Y.	20.90	18.50	20.60	20.10	20.87
H. M. Shilstone, New Orleans, La.	21.10	20.37	20.70
Average.....	21.44	20.81	20.37	21.12	17.48	20.60	19.76	20.25

Taking first of all the results on the refractometric method, it will be seen that the work entirely confirms the results obtained in previous years, proving that the error brought about by diluting the dark-colored solution is reduced to a minimum by using a sugar solution as a diluent. To investigate this question

further, a number of other samples were tested by a small number of cooperators, working on the same instrument, thereby making conditions as nearly as possible uniform throughout the work. The results of this are shown in Table 2.

TABLE 2.—*Moisture determinations with the refractometer.*

Description of sample.	Name of analyst.	Undiluted.	Diluted with water.	Diluted with sugar solution.
		<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
Sample B: Second molasses.....	W. E. Cross.....	20.75	18.76	20.50
	H. M. Shilstone.....	21.05	19.70	20.10
	W. G. Taggart.....	21.00	20.50	20.87
Average.....		20.93	19.65	20.49
Sample C: First molasses.....	W. E. Cross.....	20.93	19.70	21.09
	W. G. Taggart.....	21.40	21.10	21.57
	H. M. Shilstone.....	21.10	20.37	20.70
Average.....		21.14	20.39	21.12
Sample D: Sirup.....	W. E. Cross.....	35.65	35.20	35.57
	H. M. Shilstone.....	36.40	36.32	36.12
Average.....		36.02	35.76	35.85
General average.....		24.78	23.95	24.57

These results are in entire agreement with those obtained last year, as the following table shows:

TABLE 3.—*Comparison of moisture data obtained in 1910 and 1911.*

Data.	Undiluted.	Diluted with water.	Diluted sugar solution.
1910 average (4 samples).....	24.71	23.82	24.09
1911 average from Table 1.....	20.60	19.76	20.25
1911 average from Table 2.....	24.78	23.95	24.57

In all of these determinations it is shown that by using a molasses diluted with sugar solution the results obtained more nearly approximate the true refractometric reading—i. e., on the undiluted solution—than when water is used as a diluent. As this is also, of course, in full accord with theoretical reasoning, it would appear desirable to modify the “provisionally” prescribed method by stating that when dilution is necessary a sugar solution should be used.

Another point brought out by the figures of this year, as well as by those of previous years, is the fact that the official aerometric method with the Brix spindle gives results which are entirely removed from what the drying and refractometric methods indicate to be the true values. The following table shows this very clearly.

TABLE 4.—*Total solids by Brix compared with results by other methods.*

Substance.	Drying at 100° C. 10 hours (average).	Drying in vacuum.	Refracto- meter.	Average.	Brix.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	
A: First centrifugal molasses (1911).....	78.88	79.63	79.40	79.30	82.52
B: High-grade sirup (1910).....	73.54	72.82	73.03	73.13	74.05
C: High-grade open-kettle molasses (1910).....	74.53	73.71	74.51	74.25	75.21
D: Centrifugal molasses (1910).....	74.11	73.83	74.70	74.21	76.20
E: Mixture of blackstrap and glucose.....	77.59	77.81	78.92	78.11	83.33

We are taught by all scientific opinion and practice to consider the results obtained by the drying method (and especially the drying vacuum method) as the closest approximation to the correct value, and the refractometric results also support this view. It, therefore, seems that the Brix spindle method gives results which are very far from correct, and there is no apparent reason why this method should, in face of this evidence, continue as an official method. I believe I am right in saying that samples C and D of Table 4 would afford ground for prosecution under the pure food law, although the Brix value is higher than 75 per cent in each case.¹

Another question of importance is the necessity or otherwise of the use of sand in the drying method. It is the custom in very many laboratories to determine moisture by the simple heating for 10 hours without sand; in fact, I believe I am right in stating that the method of drying with sand has only entered into routine work to a very small extent. In the following table the average results obtained by heating 10 hours with and without sand are compared.

TABLE 5.—*Moisture determinations with and without sand.*

Sample.	With sand.	Without sand.
	<i>Per cent.</i>	<i>Per cent.</i>
Molasses, 1911.....	21.44	20.81
Molasses, 1910.....	24.80	24.38
Sirup, 1910.....	26.60	26.33
Average.....	24.28	23.85

The results by the drying method without sand thus approximate reasonably those by the vacuum method and the method of drying with sand. In view of the comparative awkwardness of the sand-drying method, and of the extensive use of the method of drying without sand, it might seem desirable to give some sort of recognition to the latter method.

MOISTURE CONTENT OF SUGARS.

An attempt was made to compare the ordinary method of determining the moisture content of sugar by drying with a refractometric method, in which the raw sugar was dissolved in its own weight of water and the refractive index of the solution taken. The results of the work, however, were so various that

¹ I am aware of the rider on page 65, Bulletin 107, Revised, to the effect that the aerometric method does not apply to "low-grade products," but all of the samples in Table 4, except E, are technically "high grade" products.

no conclusions whatever could be drawn therefrom, so that the question must be left over to another year.

TABLE 6.—*Moisture in raw sugars.*

Name.	By official method.	By refractometer.
	<i>Per cent.</i>	<i>Per cent.</i>
W. G. Taggart, New Orleans, La.	1.09	0.48
S. F. Sherwood, Washington, D. C.	1.16	.86
R. S. Hiltner, Denver, Colo.	1.00	.30
G. H. Hardin, New York, N. Y.	1.05	1.10

POLARIZATION.

The work of last year showed that the use of Horne's dry lead subacetate as a clarifying agent gave results almost identical with those obtained with lead subacetate solution. This question was further investigated this year and the results are given in Table 7.

TABLE 7.—*Polarization results using normal quantity of clarifying agents.*

Names.	Lead subacetate.				Horne's dry lead.				Molasses.	
	Molasse..		Sugar.		Molasses.		Sugar.		Meth- od 3.	Meth- od 3a.
	Single.	Clerget.	Single.	Clerget.	Single.	Clerget.	Single.	Clerget.		
A. Given, Washing- ton, D. C.	31.00	38.66	96.50	96.51	20.50	38.74	96.35	97.00	31.00	31.00
S. F. Sherwood, Washington, D. C.	31.20	39.19	96.60	96.38	96.50	96.03	30.90	30.80
W. D. Horne, New York, N. Y.	30.80	38.92	96.38	96.36	30.80	38.42	96.12	96.16	30.38
H. Z. E. Perkins, New Orleans, La.	95.78	95.55	95.68	95.37	32.05	31.68
B. J. W. Pearce, New Orleans, La.	31.60	38.53	95.90	96.35	31.64	38.70	95.88	96.06	31.19	31.70
W. H. Hoffman, Jr., New Orleans, La.	31.20	38.03	96.00	96.50	31.20	38.80	96.20	97.31	31.24	31.24
W. E. Cross, New Orleans, La.	32.20	39.35	96.40	97.73	32.32	39.33	96.25	97.57	31.57	31.68
W. G. Taggart, New Orleans, La.	32.00	39.65	96.35	97.88	32.00	39.38	96.35	97.79	31.80	31.85
R. S. Hiltner, Den- ver, Colo.	29.70	37.90	95.57	97.30	29.90	37.50	95.57	96.60	30.20	30.36
Average.....	31.21	38.78	96.16	96.73	31.19	38.69	96.10	96.65	31.17	31.29

SUMMARY OF AVERAGE RESULTS.

Methods.	Molasses.		Sugar.	
	Single.	Clerget.	Single.	Clerget.
Dry lead.....	31.19	38.69	96.10	96.65
Lead subacetate solution.....	31.21	38.78	96.16	96.73
Difference.....	-.02	-.09	-.06	-.08

These results confirm those of previous years, showing that, properly employed, the Horne's dry-lead method gives results practically identical with those of the standard method. In previous years the proposal has been made that

the dry-lead method should be made the sole official one, as it has the advantage of eliminating the error due to the lead precipitate. While the evidence would seem to show that this step is justified, the writer feels that as it is against or, shall we say in advance of, almost all home and foreign practice, very careful consideration should be given to the matter before the recommendation is adopted.

The work on the polarization of molasses by methods 3 and 3a was intended to investigate the effect of removing the error due to the influence of the alkaline lead solution on the specific rotation of the levulose present. Unless there was a considerable excess of lead there would be no levulose removed in the precipitate; and as the filtrate was restored to slight acidity with acetic acid, the levulose would have its normal value. However, as is seen from Table 7, almost identical results were obtained with this as with the ordinary method.

On account of pressure of other matters, it was found impossible to carry out any work on recommendations 2 and 4 of last year.

RECOMMENDATIONS.

It is recommended—

(1) That Herles's solution and neutral lead acetate be adopted provisionally as clarifying agents.¹

(2) That the provisionally adopted method for the refractometric determination of moisture in molasses, etc., should include instructions to dilute the molasses with a pure sucrose solution, instead of water, when the molasses is too dark to allow of direct reading.

(3) That, since the official areometric method of determining "total solids" gives with all molasses, sirups, etc., results which are admittedly too high, the advisability of retaining this as an official method should be considered.

(4) That consideration should be given to the advisability of giving some recognition to the method of drying molasses without sand, a method which is widely used in actual work and which gives results which approximate fairly closely those of the provisionally adopted drying method.

(5) That the advisability of adopting Horne's dry-lead clarification as the sole official method be discussed.

(6) That further work should be done on the determination of moisture in sugars by means of the refractometer, on the influence of the composition of the basic lead acetate (as clarifying agent) on the polarization of sugar solutions, and on the factors used in the formula for determining commercial glucose.

TEMPERATURE CORRECTIONS IN RAW SUGAR POLARIZATIONS.

By W. D. HORNE.

In polarizing raw sugars at temperatures other than the standard 20° C. errors are introduced that are of serious moment. Much has been written on the subject, and temperature corrections have been worked out, but unfortunately they have not been generally adopted. One of the best methods of effecting the necessary corrections is that described by C. A. Browne at the Seventh International Congress of Applied Chemistry, to be described later; and the present paper is to present results on many hundreds of analyses, which entirely corroborate the reliability of this method of correction.

¹ This recommendation was sent in last year, but arrived too late to be considered by the committee. The present referee regards the results of last (and previous) year's work on these clarifying agents as entirely justifying this recommendation.

In the spring of 1909, when the New York Sugar Trade Laboratory was planned, I made some preliminary experiments on temperature corrections in my own laboratory to ascertain the relative results of polarizing at 20° C. and at higher temperatures, and later I have made continued close comparisons between the polarizations of the Sugar Trade Laboratory at 20° C. and the polarization of the same sugars in other laboratories at ordinary room temperatures.

In the early experiments it was necessary, for polarizing at 20° C.—

(1) That the solution of the normal weight of sugar should be made up to 100 cc at 20° C.

(2) That it should be polarized at 20° C.

(3) That the polariscope should be at 20° C.

In order to accomplish these ends I cooled the solution of sugar, in a flask containing a thermometer, in ice water to 20° C., filling to the mark with a few drops of water at about this same temperature. The solution was then shaken and filtered at room temperature, which necessarily warmed it up a little, as the laboratory was usually above 20° C. This filtrate was put into a tubulated 200 mm observation tube, containing a centrally located thermometer, and immersed in ice water until the temperature fell a little below 20° C. (about 18°), dried with a towel, two protecting caps containing granular soda lime to prevent condensation of atmospheric moisture on the cold end glasses were slipped on, and the whole was put into the polariscope. These caps fit tightly over the ends of the observation tube, each having a glass-windowed end and an annular space inside filled with soda lime, which was found to be much better for this purpose than calcium chlorid or caustic alkali.

The polariscope was kept at 20° C. by inclosing the working parts, including both polarizing and analyzing nicols, in a galvanized-iron box covered with a $\frac{5}{8}$ -inch layer of cork board and containing two $\frac{1}{4}$ -inch copper tubes running along each side of the inside of the box, through which ice-cold water was circulated.

It was found advisable to pass water at 1° C. through this tube at the rate of 100 cc per minute, which cooled the polariscope to 20° C., as shown by a thermometer passing through the box and covering near the analyzer and compensating quartz wedges. The water issued at about 13° C. when the temperature of the room was between 23° and 31° C. The polariscope was maintained at 20° C. about an hour before polarizations were made, and the observation tube when inserted at other temperatures than 20° quickly came to this standard, a change of as much as two degrees taking place in four minutes.

Cane sugars polarized at temperatures higher than 20° C. are subject to a temperature correction which may be divided into two parts: (1) The temperature correction for pure sucrose, given by the formula $P_{20} = P^t [1. + 0.0003 (t - 20)]$, and (2) the temperature correction as applied to pure levulose, the formula being $P_{20} = P^t - 0.00812 L (t - 20)$. By properly applying the combination of these formulas to a raw-cane sugar polarized at temperatures other than 20°, it is possible to arrive at a result very close indeed to that which would be obtained when polarizing the sugars at 20°, as may be seen by the following set of observations on eight raw sugars, giving the polarizations actually obtained at 20° C. (the polariscope, the solution, and containers all being at this same degree), and polarizations of the same sugars at higher degrees (Table 1). These 95° sugars were assumed to contain 1.25 per cent invert sugar on the average, and having calculated the corrections for the sucrose and levulose separately and united all of these results, it was found that the corrected polarizations were only 0.0247 of a polariscopic degree lower than the polarizations actually made at 20° C.

TABLE 1.—*Comparison of calculated polarization of eight raw sugars with actual polarization at 20° C.*

Temperature (° C.) and polarization (° V.).		Difference in polarization.	Calculated correction—			Difference of calculated polarization from actual polarization at 20° C.
			For sucrose alone.	For levulose.	For both levulose and sucrose.	
At 20° C.:	At 26.5° C. ° V.:					
95.4.....	95.3.....	—0.10	+0.1868	—0.0330	+0.1538	+0.0538
At 21° C.:						
95.5.....	95.25.....	— .25	+ .1572	— .0279	+ .1293	— .1207
95.5.....	95.2.....	— .30	+ .1571	— .0279	+ .1292	— .1708
95.3.....	95.15.....	— .15	+ .1570	— .0279	+ .1291	— .0209
At 20° C.:						
95.3.....	95.15.....	— .15	+ .1855	— .0330	+ .1525	+ .0025
95.5.....	95.4.....	— .10	+ .1862	— .0330	+ .1532	+ .0532
95.3.....	95.2.....	— .10	+ .1855	— .0330	+ .1525	+ .0525
95.2.....	95.0.....	— .20	+ .1856	— .0330	+ .1526	— .0476
Average.....						— .0247

As the invert sugar content of these sugars was not definitely known, a further investigation of 12 samples of raw sugar was made in which the invert sugar content of each was accurately determined, giving the results shown in Table 2.

TABLE 2.—*Further comparison of calculated and observed polarizations on twelve samples of raw sugar whose invert sugar content was known.*

Temperature (° C.) and polarization (° V.).		Difference in polarization.	Calculated correction for sucrose alone.	Invert sugar.	Calculated correction for levulose alone.	Combined corrections.	Difference of calculated polarization from polarization at 20°.
At 20°:	At 28°:						
95.25.....	95.1.....	—0.15	+0.2282	1.33	—0.0432	+0.1850	+0.0350
85.80.....	85.7.....	— .10	+ .2057	2.50	— .0812	+ .1245	+ .0245
94.25.....	94.0.....	— .25	+ .2256	1.45	— .0471	+ .1785	— .0715
94.3.....	94.1.....	— .20	+ .2258	1.39	— .0451	+ .1807	— .0183
	At 25°:						
93.5.....	93.3.....	— .20	+ .1400	1.84	— .0374	+ .1026	— .0974
94.7.....	94.55.....	— .15	+ .1418	.81	— .0164	+ .1254	— .0246
85.8.....	85.7.....	— .10	+ .1286	1.77	— .0359	+ .0927	— .0073
94.7.....	94.6.....	— .10	+ .1419	1.07	— .0217	+ .1202	+ .0202
94.6.....	94.4.....	— .20	+ .1416	1.45	— .0294	+ .1122	— .0878
	At 27°:						
87.6.....	87.6.....	— .00	+ .1839	2.15	— .0595	+ .1244	¹ — .1244
95.3.....	95.15.....	— .15	+ .2001	.91	— .0260	+ .1741	+ .0241
94.6.....	94.4.....	— .20	+ .1998	1.48	— .0421	+ .1577	— .0423
First average.....							— .0101
Second average.....							— .0205

¹ Excluded from second average.

Having applied the formulas for correction of sucrose and levulose, the results obtained in the last column show the differences of the polarizations made at high temperatures and calculated back to 20° from the polarizations actually made at that temperature. The average of 12 such determinations gives a result for the sugars polarized above 20° of only 0.0101 polariscopic degrees lower than the polarizations actually made at 20° C. Omitting the tenth sample in this series, which seems to be irregular, we find that the average calculated polarization is only 0.0205 polariscopic degrees lower than the polarization actually made at 20°. These observations are quite in accord with those made

by Browne, on mixtures containing known amounts of sucrose and levulose in raw-sugars and molasses and reported by him in the article above cited.

In order to get a further comparison between polarizations made at 20° C. and those made at higher temperatures and calculated at 20° C., I have made monthly comparisons between the polarizations of many hundreds of samples tested both at the Sugar Trade Laboratory and at other laboratories.

By use of the formulas above given, the polarization of all the raw sugars coming to two technical laboratories have been arranged in groups covering monthly periods, corrected for temperature and compared with the corresponding average polarizations obtained in the Sugar Trade Laboratory when tested at 20° C.

The results found are expressed in the following table, which gives in decimal fractions of a single polariscopic degree the variations of my Laboratory "A" and Laboratory "B" results, after calculating to 20° C., from the results obtained in the Sugar Trade Laboratory when conducting the whole operation at 20° C.

TABLE 3.—Variations in two laboratories where results were corrected for temperature from Trade Laboratory results obtained at 20° C.

Date.	Corrections for Laboratory "A."			Differ- ence from Trade Labora- tory.	Corrections for Laboratory "B."			Differ- ence from Trade Labora- tory.
	Sucrose.	Levulose.	Total.		Sucrose.	Levulose.	Total.	
1911.								
March.....	+0.0800	-0.0140	+0.0660	-0.0070	+0.0424	-0.0059	+0.0365	-0.0096
April.....	+ .1290	- .0236	+ .1054	+ .0140	+ .0239	- .0036	+ .0203	+ .0200
May.....	+ .2002	- .0303	+ .1699	+ .1190	+ .0990	- .0180	+ .0810	+ .0710
June.....	+ .1977	- .0575	+ .1402	+ .0436	+ .1832	- .0355	+ .1477	+ .0117
July.....	+ .2235	- .0576	+ .1659	+ .0273	+ .2373	- .0580	+ .1793	- .0170
August.....	+ .2329	- .0634	+ .1695	- .0625	+ .1177	- .0344	+ .0833	+ .0193
September.....	+ .1379	- .0373	+ .1006	+ .0047	+ .1666	- .0520	+ .1146	- .0267
Average corrections for both laboratories.....					+ .1486	- .0351	+ .1135	+ .0148

Thus we see that the average discrepancy in this series of about 1,000 samples is only +0.0148 polariscopic degree, but if the levulose correction had not been applied this quantity would be increased to +0.0499.

The levulose correction is thus twice as great as the total experimental error and should by no means be ignored. The ideal method is, of course, to conduct the entire operation of polarizing sugars at 20° C., but as this requires an expensive plant or somewhat increased work and time by the method outlined, cases will arise where a temperature correction will be required. My contention is that if any such correction is to be applied it should be done in accord with a full appreciation of the significance of levulose as well as of sucrose and thus be made as correct as our present knowledge will allow.

REPORT OF COMMITTEE B ON RECOMMENDATIONS OF REFEREES.

By E. M. CHACE, *Chairman*.

(Dairy products, foods and feeding stuffs, sugar, tannin, and medicinal plants and drugs.)

FOODS AND FEEDING STUFFS.

It is recommended—

(1) That the method for acidity suggested by the referee for provisional adoption, together with the method of reporting results, be studied for another year. (See pp. 198, 201.)

Adopted.

(2) That the petroleum ether methods for fat, of the Cotton Seed Crushers Association, as given in the report of the referee, be printed and studied further. (See p. 198.)

Adopted.

(3) That the study of the modification of the official method for crude fiber be discontinued.

Adopted.

(4) That the study of the proper factor for converting nitrogen into protein be continued.

Adopted.

SUGAR.

It is recommended—

(1) That Herles's solution and neutral lead acetate be adopted provisionally as clarifying agents in polarizing cane products.

Finally adopted as provisional.

These methods have been formulated as follows:

Neutral lead acetate.—Prepare a saturated solution of normal lead acetate and, as in the case of the basic lead acetate solution, add it to the sugar solution before completing to volume. Its use is imperative when determining the reducing sugars in the solution used for polarization.

Basic lead nitrate (Herles's solution).—(1) Dissolve 250 grams of lead nitrate in water and make up to 500 cc. (2) Dissolve 25 grams of sodium hydroxid in water and make up to 500 cc.

Add equal amounts of the two solutions (1) and (2) to the sugar solution, shake, and add more if sufficient precipitation has not occurred, taking care not to add an excess. Then complete the volume with water. When this solution is used for clarification, the factor in the Clerget determination becomes 143.5 instead of 142.66.

(2) That the provisional method for the determination of moisture in molasses by the refractometer be amended so as to provide for the use of a pure sucrose solution instead of water for diluting samples too dark to read. (Bul. 132, p. 178.)

Adopted.

(3) That to the official aerometric method for the determination of total solids (Bul. 107, Rev., p. 65) a note be added to the effect that the results on molasses and other materials containing large amounts of invert sugar or nonsugar solids are only roughly approximate.

Approved and referred for final adoption in 1912.

(4) That it be noted that Horne's dry lead clarification method is not an optional method but is provisional and has the same standing as the wet clarification method. (Bul. 132, p. 189, and Bul. 107, Rev., p. 40.)

Adopted.

This method reads as follows:

Dry lead subacetate (Horne's method).—This clarifying agent is obtained as a dry powdered salt and should contain 72.8 per cent of lead, which corresponds to a composition of $3\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{PbO}$. Dissolve the normal or half-normal weight of the sugar solution in a flask with water and complete the volume. Add a small quantity of the dry salt and shake, then add more and shake again, repeating until a point of sufficient precipitation is reached to allow of an easy reading. An excess is to be avoided. Of this salt 0.1346 gram is equivalent to 1 cc of the solution of subacetate described under lead subacetate solution. When molasses or any other substance producing a heavy precipitate is being clarified, some dry, coarse sand should be added to break up the balls of lead subacetate and precipitate. (This method is to have equal weight with the use of a solution of lead subacetate in clarifying cane, sorghum, and beet products.)

(5) That the referee's recommendation as to future study be adopted, i. e., that further work should be done on the determination of moisture in sugars by means of the refractometer. on the influence of the composition of the basic lead acetate (as clarifying agent) on the polarization of sugar solutions, and on the factors used in the formula for determining commercial glucose.

Adopted.

TANNIN.

It is recommended—

(1) That the methods for the analysis of leather proposed for provisional adoption by the referee be printed with the view to subsequent adoption (see page 231).

Adopted.

MEDICINAL PLANTS AND DRUGS.

It is recommended—

(1) That the recommendation of the associate referee as to further study of methods for mixtures of acetphenetidin and salicylates be adopted.

Adopted.

(2) That the following minor changes be made in the provisional method for caffeine (Bul. 132, p. 197): That the size of the flasks in lines 3, 13, and 23 be changed from 100 cc to 200 cc; that in line 11 "Add 4 times the volume, in this case 80 cc" be changed to "Add 3 times the volume, in this case 60 cc"; that in line 15 "for a second extraction" be changed to "for a second and third extraction."

Approved and referred to association for final adoption in 1912.

(3) That the work on medicated soft drinks be continued.

Adopted.

(4) That the work on medicinal plants and drugs be continued.

Adopted.

REPORT OF THE AUDITING COMMITTEE.

The auditing committee has examined the accounts of the treasurer and find them to be correct.

[Signed] J. M. BARTLETT, *Chairman*,
BURT L. HARTWELL.¹

The report of the treasurer for 1911 was, in brief, as follows, detailed statement and vouchers being filed with the records of the secretary:

RECEIPTS.

Balance from 1910.....	\$43.47
Dues from 40 stations, colleges, State chemists, etc., of \$2 each.....	80.00
Total	123.47

¹ O. M. Shedd, the third member of the committee, was not present when the report was presented

EXPENDITURES.

December 20, 1910, to the Nittany Printing and Publishing Co. (for printing of food standards committee, as ordered by the association) --	\$43.47
January 30, 1911, 400 circulars and 250 envelopes (dues and collaboration) -----	7.25
Postage on same -----	3.00
August 30, 1911, 550 circulars and 200 envelopes (call for meeting and program) -----	14.25
Postage on same -----	2.18
Miscellaneous postage -----	1.14
Total -----	71.29
Balance -----	52.18

NOVEMBER 13, 1911.

REPORT OF THE COMMITTEE ON RESOLUTIONS.

The following report was submitted by William Frear, as chairman of the committee on resolutions:

Resolved, That this association hereby expresses its appreciation to President Woll for the able, impartial, and courteous manner in which he has presided over its deliberations.

Resolved, That the association hereby thanks the secretary of the association, Dr. H. W. Wiley, for his continuance of the service to which the association so largely owes its vigor and efficiency.

Resolved, That this association is grateful to the Secretary of Agriculture for his renewed expression of encouragement to, and assurance of cooperation with, the association in its work.

Resolved, That this association hereby expresses its high appreciation of the courtesies extended to its members by the Cosmos Club and the Washington Section of the American Chemical Society.

Resolved, That the secretary of the association be instructed to communicate to the parties and organizations concerned copies of the foregoing resolutions.

Adopted.

Mr. Haskins called attention to the fact that no report had as yet been made by the special committee appointed in 1909 to study the availability of phosphoric acid in basic slag phosphate by means of vegetation experiments; and inasmuch as the work was of great importance it was moved that the committee be discharged and a new committee appointed. The motion was carried. (See p. 252 for personnel of committee.)

REPORT ON MEAT AND FISH.

By RALPH HOAGLAND, *Associate Referee*.¹

INTRODUCTION.

In order to get the opinion of various food chemists as to what problems in connection with the adulteration of meat and fish seemed worthy of investiga-

¹ Presented by A. S. Mitchell.

tion. letters were sent out early in the summer to a number of chemists asking for suggestions. The following problems were proposed:

- (1) Determination of starch in sausage.
- (2) Detection of incipient putrefaction in meats.
- (3) Determination of tin in canned goods.

All three of these problems need attention, but the third was selected for cooperative work.

Mayerhofer's method for the determination of starch in sausage, as given in Bulletin 107, Revised, Bureau of Chemistry, is tedious, inaccurate, and generally unsatisfactory, as the writer has learned from several months' experience with the method. A more rapid and accurate method for the determination of starch in meat products is much needed, owing to the widespread use of starch in sausages.

The second problem, that of methods for the detection of incipient putrefaction in meat products, is of great importance, but demands long-continued investigation by those particularly fitted for that kind of work, rather than cooperative work, at this time.

The Federal Board of Food and Drug Inspection has placed a limit of 300 mg of tin per kilo in canned goods; hence the importance of a rapid and accurate method for determination of tin in such products.

R. E. Doolittle, then in charge of the Food and Drug Inspection Laboratory, New York City, suggested the problem and also the method which has been used in the cooperative work. He stated that he had found the method for determination of heavy metals in canned goods, Bulletin 107, Revised, tedious and unreliable, as have also Schreiber and Taber. (See Circular 67, Bureau of Chemistry.) Doolittle also states that he has found Schreiber and Taber's sulphuric acid digestion method, as described in the circular mentioned, rather too time consuming, and needing too much personal attention for inspection work.

The method proposed by Doolittle and Lourie, and which they state has given excellent satisfaction in routine work, was incorporated in the following letter sent out to cooperators:

INSTRUCTIONS FOR COLLABORATIVE WORK.

*The determination of tin in canned food products (Doolittle and Lourie).—*Place 25 to 50 grams of the well-mixed and finely ground sample in a Kjeldahl flask (800–1,000 cc) and add 25 to 50 cc of concentrated sulphuric acid, the amount depending upon the weight of the charge. Place the flask on a hot plate or on wire gauze over free flame; add about 30 cc of concentrated nitric acid, raise temperature to boil, and heat till white fumes are generated, then without cooling add 10 cc of nitric acid and continue heating as before. Repeat the nitric acid addition until the solution remains clear (usually straw color) after boiling off the nitric acid fumes. The digestion can easily be accomplished in three hours with from three to four additions of the acid. Let the solution cool and dilute to about 400 cc with water. Nearly neutralize with concentrated ammonium hydroxid, transfer the solution to a beaker, saturate with hydrogen sulphid, and let the precipitate settle on a steam bath. Filter, wash the precipitate with a little hot water saturated with hydrogen sulphid, and then dissolve it in hot yellow ammonium sulphid; reprecipitate with acetic acid or hydrochloric acid, filter on ashless paper, ignite and weigh as stannic oxid (SnO_2). Finally moisten with nitric acid. (NOTE.—50 cc of concentrated ammonium hydroxid will nearly neutralize 25 of concentrated sulphuric acid. Make the usual tests for the complete precipitation in the filtrate from the first tin sulphid precipitate. In the case of canned vegetables as high as 100 grams may be taken without using more than 50 cc of sulphuric acid. With fish it is best to use as many cubic centimeters of sulphuric acid as grams of fish. The rapidity of the digestion depends on the temperature maintained—the higher the temperature the faster the material is oxidized.)

Samples to be analyzed.—A sample of stannous chlorid is being mailed you under separate cover for use in this work.

All determinations are to be made in *duplicate*, and individual as well as average results should be reported.

1. Weigh into three Kjeldahl flasks, respectively, 20, 30, and 50 mg of the stannous chlorid, and then to each flask add 50 grams of finely ground fresh meat; proceed with the determination as directed.

2. Procure approximately 1-pound cans of the following products: roast beef, rhubarb, pumpkin.

Preparation of sample.—In the case of meat run the product twice through a meat grinder and then mix thoroughly with the liquid portion. In the case of rhubarb macerate the solid portion and make a uniform mixture with the juice.

Use 50 grams of each product for the determination. In case a very small amount of tin is obtained repeat the operation, using a larger quantity of material.

If the products mentioned are not obtainable, get similar products which will include a meat, fruit, and vegetable. * * *

ANALYTICAL RESULTS.

Results obtained by the nitric-acid method when known amounts of tin were added to meat.

Analyst.	Stannous chlorid added.	Stannic oxid added.	Stannic oxid recovered.	Average.
	<i>Mg.</i>	<i>Mg.</i>	<i>Mg.</i>	<i>Mg.</i>
H. Schreiber and W. C. Taber, Washington, D. C.	20	10.6 10.6 15.9	10.6 10.5 14.8	10.55
	30	15.9 15.9 26.5	15.8 15.8 25.4	15.3
	50	26.5 26.5 9.9	25.3 25.3 9.6	25.35
H. L. Lourie, ¹ New York City.	20	9.9 9.9 14.8	9.6 9.6 15.3	9.6
	30	14.8 14.8 24.6	14.4 14.4 25.0	14.85
	50	24.6 24.6 24.3	24.3 24.3 24.3	24.65

¹ Did not add exactly 20, 30, and 50 mg of tin salt; calculated to comparable basis.

Mr. Lourie's analysis of the tin salt showed 49.3 per cent of stannic oxid and 38.85 per cent of tin. Schreiber and Taber's analysis gave 53 per cent of the oxid.

Schreiber and Taber made an interesting comparative study of the nitric-acid method (Doolittle and Lourie) and the sulphuric-acid method (Schreiber and Taber) for the determination of tin in various products, with the following results:

Results by both methods when known amounts of tin salt were added to 50 grams of corned beef (Schreiber and Taber).

Stannic oxid added.	Stannic oxid already in beef. ¹	Total stan- nic oxid calculated as present.	Total stan- nic oxid found.
<i>Gram.</i>	<i>Gram.</i>	<i>Gram.</i>	<i>Gram.</i>
0.0132	0.0048	0.0180	¹ 0.0189
.0134	.0048	.0182	1.0198
.0124	.0048	.0172	2.0179
.0117	.0048	.0165	2.0161

¹ Sulphuric acid method.

² Nitric acid method.

*Results by Schreiber and Taber on tin in various commercial canned products,
by both methods.*

[Expressed in grams of tin per 100 grams of sample.]

Sample.	Nitric acid method.	Sulphuric acid method.
Rhubarb.....	{ 0.0469 } 0.0479	{ 0.0492 } 0.0493
Gooseberries.....	{ .0223 } .0222	{ .0254 } .0267
Strawberries.....	{ .0217 } .0221	{ .0198 } .0221
Pumpkin.....	{ 1.0569 } .0570	{ .0560 } .0530
Mustard sardines.....	{ 1.1544 } .1634	{ 1.1571 } .1567
Mustard sardines plus sodium chlorid.....	{ 1.1620 } .1550	{ 1.1505 } .1578
	{ 1.1481 }	{ 1.1652 }

¹ 50-gram sample used in these determinations; all others were 100-gram samples.

Lourie reports the following results of analyses of canned goods for tin at the New York Food and Drug Inspection Laboratory by the nitric-acid method, unless otherwise noted:

Tin found in various types of canned goods in routine work in New York Laboratory.

Sample No.	Substance.	Amount of tin found.
		<i>Mg per kilo.</i>
N. Y. 21386.....	Tomato herring.....	183.0
N. Y. 21387.....	do.....	105.0
N. Y. 21389.....	do.....	446.0
N. Y. 21410.....	do.....	189.9
N. Y. 21411.....	do.....	551.0
N. Y. 21427.....	do.....	217.0
N. Y. 21428.....	do.....	169.0
N. Y. 21264.....	do.....	407.4
N. Y. 21266.....	do.....	134.7
N. Y. 21267.....	do.....	494.9
N. Y. 21268.....	do.....	116.0
N. Y. 21269.....	do.....	116.0
N. Y. 21280.....	do.....	472.0
Check ¹	do.....	340.4
Check ¹	do.....	327.8
Check ²	do.....	275.1
N. Y. 24783.....	do.....	539.4
N. Y. 24783 ¹	do.....	554.8
N. Y. 21855.....	do.....	255.0
N. Y. 21836.....	do.....	58.3
N. Y. 21289.....	Herring.....	235.0
N. Y. 21290.....	do.....	96.0
N. Y. 21291.....	do.....	78.8
N. Y. 21244.....	do.....	285.0
N. Y. 21245.....	do.....	278.0
N. Y. 21246.....	do.....	539.0
N. Y. 21247.....	do.....	523.0
N. Y. 21592.....	do.....	312.0
N. Y. 21580.....	do.....	60.0
N. Y. 21579.....	do.....	121.0
N. Y. 21876.....	do.....	61.0
N. Y. 21783.....	Kippered herring.....	504.0
N. Y. 21782.....	Soused mackerel.....	66.2
N. Y. 21861.....	W. I. spiny lobster.....	51.2
N. Y. 21443.....	Apricot pulp.....	157.0
N. Y.....	Sardines.....	530.0
N. Y. 27384.....	Mixed vegetables.....	230.0
I. S. 3446.....	Apple butter.....	677.8
N. Y. 21390.....	Cockles.....	5.0
N. Y. 21443.....	Sardines in tomato sauce.....	443.0
N. Y. 21487.....	do.....	654.0
N. Y. 21243.....	Sorrel.....	70.0
N. Y. 24429.....	Herring in bouillon, can 1.....	528.0
	Herring in bouillon, can 2.....	506.0
N. Y. 24582.....	Vegetables in vinegar.....	104.8
N. Y. 24738:		
No. 1 ²	Herrings in bouillon.....	219.1
No. 1 ¹	do.....	409.8
No. 2 ¹	do.....	892.8
No. 2 ¹	do.....	819.6
No. 2 ²	do.....	434.2

¹ Oxidation method.

² Munson method.

COMMENTS ON RESULTS.

The results of the cooperative work on Lourie's method for the determination of tin in canned goods are quite satisfactory, duplicate determinations checking well, while the results of the two cooperators check closely, considering the comparatively small quantities of tin which are recovered.

Schreiber and Taber find that results by the sulphuric-acid and the nitric-acid (Lourie) methods agree very closely.

I have tried out Lourie's method in a preliminary way and find that with constant attention complete digestion of 50 grams of meat can be accomplished in a little over two hours. Doubtless the time for digestion of other materials will vary one way or the other. After the complete digestion of the material one has to observe only the precaution necessary for the determination of tin.

Schreiber and Taber have the following additional comments to make regarding Doolittle and Lourie's method for the determination of tin in canned goods:

Schreiber and Taber: From results of our work it would seem that the nitric acid method gives as good results as the sulphuric acid digestion method, and that it recovers all the tin in the sample.

Some of the disadvantages of the proposed nitric acid method might be mentioned. The noxious oxides of sulphuric acid and organic matter form a very disagreeable feature. Then it was found that meats or fish require for their complete digestion, instead of the three or four additions of nitric acid as mentioned in the method, at least twice that number. It was also found in our work that it is not safe to add the nitric acid to the hot mass in the flask, as stated in the method, as there is great danger of frothing, and the sample running out of the flask, especially in the first stages of the digestion.

We believe that ammonium sulphid is not the best solvent to use in dissolving the tin sulphid. When the solvent is used, the subsequent neutralization of the solution is slow and tedious, as the exact strength of the sulphid employed is unknown, and the solution must not be made too acid in precipitating the tin or some will be lost. Again large quantities of sulphur are thrown down which become troublesome in the subsequent filtration, running through the filter, so that one can not tell whether or not a loss of the precipitate is taking place.

In our method for tin determination given in Circular 67, Bureau of Chemistry, potassium hydroxid (20 grams in 100 cc of water), was used as a solvent for a tin sulphid. This we have found to give as accurate results besides permitting the accurate and quick neutralization of a solution for the precipitation of the tin; it also does away with the large sulphur precipitate.

In the determinations given, potassium hydroxid was used to dissolve the tin sulphids in the sulphuric acid method and ammonium sulphid in the nitric acid method.

Concerning the time of digestion, an accurate account was kept for the two methods. In twelve determinations given in Table 3, those run by the nitric acid method were all finished in two hours; those by the sulphuric acid method, in four and one-half hours. In the second set of 12 digestions, those by the nitric acid method were finished in four hours, while those by the sulphuric acid method required four and one-half hours. On many materials it seems that the nitric acid method is shorter, but one must take into consideration that the nitric acid method requires almost continuous attention in adding more acid until the digestion is complete, while with the sulphuric acid method, after the frothing stage has passed, the sample needs no more attention.

It would seem that no one method is best for all materials and under all circumstances. The nitric acid digestion method has been used with apparent success in the laboratory.

RECOMMENDATION.

I would respectfully recommend that the associate referee on meats and fish for the next year conduct a study of the nitric and sulphuric acid methods for determination of tin in canned goods, and if results warrant, recommend one of these methods for adoption by the association as a provisional method.

REPORT ON FRUIT AND FRUIT PRODUCTS.

By A. W. BLAIR, *Associate Referee.*

INTRODUCTION.

The work on fruit and fruit products for this year was again confined to moisture determinations. Samples were prepared from green oranges (varying in diameter from $1\frac{1}{2}$ inches to $2\frac{1}{2}$ inches) as follows: Whole oranges were sliced, run through a meat chopper, and thoroughly mixed; portions were then weighed into tin-lead dishes, and dried in the air oven at 50° to 60° C. for about fifteen hours to preserve for shipping.

Chemists representing seven laboratories offered to cooperate. Five portions of the partially dried oranges, with weight of container and sample, and net weight of sample (both weights refer to the fresh sample immediately after it was prepared) together with instructions, were sent to each laboratory. Three methods were proposed as follows:

I. Water-jacketed oven: Dry in water-jacketed oven for 30 hours, or longer if necessary, weighing at the end of each six hours; report weights for each drying, and percentage for final drying. (Bul. 122, pp. 219-220).

II. Vacuum oven at 70° C.: Dry to constant weight in vacuum oven at 70° C. State length of time required. (Bul. 132, p. 150.)

III. Dry to constant weight in vacuum over c. p. sulphuric acid, without the aid of heat; state time required. (Bul. 137, pp. 138-140.)

ANALYTICAL RESULTS.

Five laboratories submitted results which are reported in the following table:

Comparison of three methods for determining moisture in fruit.

Method and analyst.	Net weight fresh sample.	Weight of con- tainer and fresh sample.	Weights on consecutive dryings.										Total loss in drying.	Mois- ture.	Aver- age.
			1	2	3	4	5	6	7	8	9	10	11	18	
(A) Water jacketed oven: A. W. Blair.....	Grams.	Grams.	Grams.	Grams.	Grams.	Grams.	Grams.	Grams.	Grams.	Grams.	Grams.	Grams.	Grams.	Grams.	P ct.
	(1) 25.8911	39.6598	18.3725	18.4190	18.3750	18.3510	18.3340	18.3160	18.2850	18.2770	18.2740	18.2740	21.1088	21.5075	83.07
	(2) 24.8779	39.9969	17.5225	17.4200	17.3775	17.3500	17.3330	17.3160	17.2900	17.2800	17.2783	17.2783	20.7184	21.4364	83.16
	(3) 26.4443	39.7402	17.8625	17.8510	17.8010	17.7745	17.7500	17.7320	17.7000	17.6920	17.6900	17.6900	22.0502	22.4364	83.20
S. E. Collison.....	(3) 23.8697	34.9125	15.2515	15.1445	15.0656	15.0699	15.0623	15.2509	15.2509	15.2509	15.2509	15.2509	19.8002	19.9499	83.18
	(2) 28.7803	34.2008	15.3673	15.3289	15.3055	15.2804	15.2625	15.2509	15.2509	15.2509	15.2509	15.2509	18.9499	18.9499	83.18
	(1) 25.3069	39.3798	18.5230	18.4190	18.3750	18.3510	18.3340	18.3160	18.2850	18.2770	18.2740	18.2740	21.1088	21.5075	83.40
	(2) 24.8779	39.9969	17.5225	17.4200	17.3775	17.3500	17.3330	17.3160	17.2900	17.2800	17.2783	17.2783	20.7184	21.4364	83.27
E. O. Eaton.....	(3) 26.4443	39.7402	17.8625	17.8510	17.8010	17.7745	17.7500	17.7320	17.7000	17.6920	17.6900	17.6900	22.0502	22.4364	83.38
	(4) 24.4899	36.8555	16.6000	16.5615	16.5250	16.5005	16.4830	16.4660	16.4400	16.4300	16.4275	16.4275	20.4280	20.8002	83.42
	(5) 25.2106	38.4854	17.7980	17.6740	17.6260	17.6000	17.5800	17.5630	17.5300	17.5230	17.5205	17.5205	20.9649	20.9649	83.16
	(1) 23.8808	35.3370	15.6800	15.6046	15.5563	15.5285	15.5285	15.5285	15.5285	15.5285	15.5285	15.5285	19.8085	19.8085	82.95
H. C. Gore.....	(2) 22.2843	33.8475	15.5185	15.4440	15.4022	15.3720	15.3720	15.3720	15.3720	15.3720	15.3720	15.3720	18.4755	18.4755	82.91
	(1) 24.3231	36.4145	16.3980	16.2770	16.2390	16.2100	16.1835	16.1600	16.1400	16.1322	16.1297	16.1297	20.2848	20.2848	83.40
	(2) 20.3369	32.5680	15.8825	15.8110	15.7735	15.7475	15.7275	15.7095	15.6915	15.6830	15.6820	15.6820	16.8860	16.8860	83.03
	24.3452	36.0292	15.9446	15.8494	15.8193	15.7960	15.7679	15.7517	15.7457	15.7319	15.7258	15.7173	15.7088	15.6695	83.62
(B) Vacuum at 70° C.: H. D. Poore..... H. C. Gore.....	23.8874	35.8300	16.3598	16.3222	16.2868	16.2671	16.2615	16.2397	16.2190	16.2091	16.2008	16.1972	16.1916	19.6384	82.21
	(1) 21.1118	32.0440	14.8474	14.8022	14.7793	14.7620	14.7620	14.7620	14.7620	14.7620	14.7620	14.7620	18.4755	18.4755	82.91
	(2) 22.3681	37.7305	19.5380	19.4894	19.4653	19.4455	19.4455	19.4455	19.4455	19.4455	19.4455	19.4455	18.4755	18.4755	82.91
	(2) 22.3681	37.7305	19.5380	19.4894	19.4653	19.4455	19.4455	19.4455	19.4455	19.4455	19.4455	19.4455	18.4755	18.4755	81.73
(C) Vacuum over sulphuric acid without heat: H. D. Poore..... A. M. Henry.....	23.6912	35.2580	15.9709	15.9502	15.9263	15.9148	15.9104	15.9034	15.8988	15.8786	15.8745	15.8623	19.3957	19.3957	81.86
	(1) 24.5273	36.4550	16.6490	16.6205	16.5730	16.5730	16.5730	16.5730	16.5730	16.5730	16.5730	16.5730	19.8820	19.8820	81.00
	(2) 21.7855	37.0655	19.4905	19.4705	19.4385	19.4385	19.4385	19.4385	19.4385	19.4385	19.4385	19.4385	17.6270	17.6270	80.98
	20.2028	32.3085	15.8337	15.8337	15.8337	15.8337	15.8337	15.8337	15.8337	15.8337	15.8337	15.8337	18.4755	18.4755	81.55
(D) Atmospheric pressure, over calcium chloride: A. M. Henry..... A. W. Blair.....	29.3263	40.4270	16.5480	16.5480	16.5480	16.5480	16.5480	16.5480	16.5480	16.5480	16.5480	16.5480	23.8790	23.8790	81.42
	(1) 24.0525	34.6445	14.8485	14.7683	14.7208	14.6870	14.6687	14.6687	14.6687	14.6687	14.6687	14.6687	19.9758	19.9758	83.05
	(2) 21.9358	32.6350	14.6104	14.5415	14.4960	14.4647	14.4470	14.4470	14.4470	14.4470	14.4470	14.4470	18.1880	18.1880	82.92
	23.3652	36.9700	17.6994	17.6288	17.5795	17.5519	17.5519	17.5519	17.5519	17.5519	17.5519	17.5519	19.4445	19.4445	83.18
S. E. Collison.....	(1) 25.3069	39.3798	18.5230	18.4190	18.3750	18.3510	18.3340	18.3160	18.2850	18.2770	18.2740	18.2740	21.1088	21.5075	83.40
	(2) 24.8779	39.9969	17.5225	17.4200	17.3775	17.3500	17.3330	17.3160	17.2900	17.2800	17.2783	17.2783	20.7184	21.4364	83.27
	(3) 26.4443	39.7402	17.8625	17.8510	17.8010	17.7745	17.7500	17.7320	17.7000	17.6920	17.6900	17.6900	22.0502	22.4364	83.38
	(4) 24.4899	36.8555	16.6000	16.5615	16.5250	16.5005	16.4830	16.4660	16.4400	16.4300	16.4275	16.4275	20.4280	20.8002	83.42

¹ Average intervals about 5½ hours.² Average intervals about 37 hours.³ Average intervals about 24 hours.

The results with the water-jacketed oven do not agree as they should. This is partly due to the fact that no two analysts dried for the same length of time, and partly, no doubt, to slight decomposition of organic materials caused by long-continued heating. It will be observed that Mr. Eaton secured fairly concordant results on four out of five samples when all were dried for the same length of time, his greatest difference on the four being 0.13 per cent when about 25 grams of fresh material were used.

The results by the vacuum methods are decidedly lower than with the water oven and are even less concordant. It will be noted that Mr. Gore's results with vacuum at 70° C. and vacuum over sulphuric acid, without the aid of heat, agree within reasonable limits, and are also in fair agreement with Mr. Poore's work by the last-named method. The fact that in most cases duplicate determinations agree within the limit of error would indicate that lack of agreement with a given method is due to differences in the time of drying.

Tests made with the electric oven at 100° C. show results in fair agreement with those obtained with the water oven. It is quite evident that the water oven, and also the electric oven, give results that are too high; that is, there is undoubtedly some loss through decomposition. This probably holds true for all fruits and fruit products containing much sugar, and points to the necessity of adopting some other method, when accurate results are desired.

Mr. Gore suggests the use of lime or barium oxid as a desiccating agent instead of sulphuric acid, to avoid the presence of the vapors of the latter in the desiccator.

It is suggested that the vacuum methods be further tested and that an effort be made to have all the work done under as nearly the same conditions as possible.

REPORT OF COMMITTEE ON NOMINATIONS.

In the absence of Mr. L. L. Van Slyke, chairman of the nominating committee, Mr. W. A. Withers presented the following report:

The following nominations are made for officers for the coming year:

President, H. J. Patterson, College Park, Md.; vice president, G. S. Fraps, College Station, Tex.; secretary, H. W. Wiley, Washington, D. C.; additional members of the executive committee: R. E. Doolittle, Washington, D. C.; A. J. Patten, East Lansing, Mich.

The secretary was instructed to cast the unanimous vote of the association for the officers as nominated.

In accordance with the resolution ordering that the referees and associates should be appointed by the outgoing executive committee rather than by the incoming committee, the president here announced the appointments made. These are given on page 251, with such subsequent changes as were necessitated by declinations, etc.

REPORT ON TANNIN.

By J. S. ROGERS, *Referee*.

PLAN OF WORK AND DESCRIPTION OF SAMPLES.

The work for this year has been designed to study certain conditions of three phases of leather analysis: (1) Shortening the time required for the extraction of fats; (2) a comparison of three methods of extraction of the soluble materials (other than fats) in leather; (3) experiments to show that basic lead acetate, when used as a clearing agent for sugar solutions in leather analysis, removes large amounts of sugar actually present.

The two samples of leather sent out were prepared as follows:

No. 1, an oak-tanned sole leather, was finely ground, allowed to come to air-dry condition, and thoroughly mixed. Moisture determinations were made and sugar was determined on the extract. A known amount of grape sugar in solution was then added to and mixed with the weighed ground leather. The mixing was continued under the blast of an electric fan until the leather was nearly dry, after which it was spread out in a thin layer to come to air-dry condition. After several days' drying in the air, the sample was reground, again allowed to come to air-dry condition, thoroughly mixed, and a moisture determination was made. Knowing the per cent of moisture and the per cent of sugar originally present, the per cent of moisture after the sugar was added, the original weight of the leather, and the weight of the sugar added, it was possible to calculate the per cent of sugar present in the prepared sample. The sugar originally present was 0.60 per cent. The calculated amount added was 7.73 per cent, giving 8.33 per cent total sugar in the prepared sample.

No. 2, an oak-tanned, heavily greased harness leather, was finely ground, spread out in a thin layer, and allowed to come to an air-dry condition.

Samples No. 1 and No. 2, as soon as prepared, were put up in quart Mason jars and tightly stoppered.

DIRECTIONS FOR LEATHER WORK.

FAT EXTRACTION.

Place 15 grams of the sample as received in an S & S thimble and extract in a Soxhlet extractor, using petroleum ether, distilling between 50° and 80° C., as directed under A, B, C, and D. Heat at such a rate that the liquid siphons approximately four times per hour.

(A) Extract two portions, 15 grams each, for 24 hours; save the leather residue; evaporate the ether from the extract on a steam bath, and dry to constant weight in a water oven; weigh and calculate the per cent of fat present. (A should be completed and the amount of fat determined before B, C, and D are started.)

(B) Extract two portions of 15 grams each for 6 hours.

(C) Extract two portions of 15 grams each for 8 hours.

(D) Extract two portions of 15 grams each for 10 hours.

Save the leather residues from B, C, and D, determine the fats in each extract as in A, and if the fat has not all been extracted in the stated time continue until the extraction is complete, noting in each case the time required and the color, consistency, and odor, and general appearance of the fat residue.

Reserve the leather residues from the fat extraction for the extraction of the uncombined tannins and nontannins, bringing them to an air-dry condition before this extraction is begun.

1. Place the two residues of A together and the two residues of B together. Use these as duplicates for the extraction by the A. L. C. A. method (E).

2. Take the two residues from C and use these as duplicates for the extraction by the method of the Bureau of Chemistry (F).

3. Take the two residues from D and use as duplicates for the extraction by the alcohol method (G).

EXTRACTION OF UNCOMBINED TANNINS AND NONTANNINS.

E. Method of A. L. C. A.—Digest the leather residues A and B as duplicates in percolators overnight, transfer the extract to a 2-liter flask, then extract with water at 50° C. for three hours, removing the extract from a side tube of the extractor, thus avoiding boiling the extract. The total volume of solution to be 2 liters. Determine the glucose, soluble solids, and nontannins as directed below:

F. Method of the Bureau of Chemistry.—Take the leather residues from C and moisten thoroughly with distilled water. Transfer leather and water to a Soxhlet extractor and place cotton above and below the leather in the extractor, to prevent it from being carried over at the time of siphoning. The cylinder of the extractor shall be surrounded by water bath kept at 50° C. At the beginning of the extraction pour 250 cc of distilled water (including that used in moistening the leather) into the Soxhlet and allow it to siphon into the flask below, then begin the boiling. At the end of the first hour remove the flame and transfer the extract to a 1-liter graduated flask, add 200 cc of distilled water to the Soxhlet and continue the extraction for two hours. Remove the extract, add 200 cc of water and continue the extraction for five hours and remove the extract. Make one more extraction, adding 200 cc as before, and continuing the extraction for six hours. This gives 14 hours' extraction and an extract that does not exceed 1 liter in volume. Make the extract up to 1 liter at room temperature, and use as directed below for the determination of glucose, soluble solids, and nontannins.

G. Alcohol method.—Take the two leather residues from D (they may be extracted in the same thimble in which the ether extraction was made after they come to an air-dry condition) and extract with 95 per cent alcohol for eight hours in a Soxhlet extractor. Add 250 cc of water to the extract and evaporate the alcohol on the steam bath, make the solution to 1 liter, at room temperature, and determine glucose, soluble solids, and nontannins as directed below.

DETERMINATION OF GLUCOSE.

(a) To 200 cc of the extract add 25 cc of a saturated solution of normal lead acetate, mix thoroughly, allow to stand about 15 minutes and filter. The funnels and beakers must be kept covered to prevent evaporation. Remove the lead from the filtrate by adding a slight excess of solid potassium oxalate and filtering. Pipette 150 cc of the last filtrate into a 600 cc Erlenmeyer flask and add 5 cc of concentrated hydrochloric acid and boil under a reflux condenser for two hours, cool, neutralize with anhydrous sodium carbonate, transfer to a 200-cc graduated flask, and make to volume. Filter through a double filter. (This filtrate must be clear.) Use 50 cc of this filtrate for the determination of sugar.

Copper-sulphate solution.—Dissolve 34.639 grams of anhydrous copper sulphate in water and dilute to 500 cc.

Alkaline tartrate solution.—Dissolve 173 grams of Rochelle salts and 125 grams of potassium hydroxid in water and dilute to 500 cc.

Place 30 cc of the copper solution, 30 cc of the alkaline tartrate solution, and 35 cc of water in a beaker and heat to boiling. Add 50 cc of the solution of the material containing the sugar, which must be so prepared as not to contain more than 0.25 grams of dextrose, and boil for two minutes. Filter immediately through asbestos without diluting, wash with hot water, alcohol, and finally with ether, dry for half an hour in a water oven, and weigh as cuprous oxid; determine the amount of dextrose by the use of Allihn's table (Bul. 107, Rev., p. 50).

(b) Determine sugar in the same manner as in (a), except that instead of using 25 cc of saturated neutral lead acetate, use 25 cc of saturated basic lead acetate.

SOLUBLE SOLIDS.

To 2 grams of kaolin in a beaker add 75 cc of extract, stir, let stand for 15 minutes, decant and discard as much as possible of the supernatant liquid, and again add 75 cc of extract to the kaolin, stir and pour at once on a No. 590 S & S folded filter, keep the filter full and the funnel and receiving vessel covered, reject the first 150 cc of the filtrate, evaporate, and dry the next 100 cc (which must be brilliantly clear). Conduct the evaporation and drying in flat-bottomed glass dishes from 2¹/₂ to 3 inches in diameter, evaporate, and

dry for 16 hours in a combined evaporator and drier from 98° to 100° C., or after evaporating dry for 12 hours on the bottom shelf of a water oven at from 98° to 100° C.

NONTANNINS.

A quantity of hide powder sufficient for the number of analyses to be made during a day shall be prepared in the following manner: Digest with 10 times its weight of water until thoroughly soaked. Add 3 per cent of chrome alum in solution, agitate by either shaking or stirring occasionally for several hours, and let stand overnight. Wash by squeezing through linen, continuing the washing until the wash water gives no precipitate with barium chlorid, squeeze the hide, using a press if necessary, so that the wet hide will contain between 70 and 75 per cent of water. Use approximately 20 grams of wet hide for moisture determination. Add to 200 cc of the original solution such quantity of wet hide as represents from 12 to 13 grams of dry hide, shake for 10 minutes in some form of mechanical shaker, and squeeze immediately through linen. Add 2 grams of the kaolin to the filtrate, stir and filter through folded filter S & S No. 590 of sufficient size to hold the entire filtrate, returning until clear, evaporating 100 cc of the filtrate. The weight of the residue must be corrected for the dilution caused by the water contained in the wet hide.

NOTE.—In order to limit the amount of dried hide powder used, determine the moisture in the air-dried hide powder and calculate the quantity equal to at least 15 grams of actual dry hide powder, take any multiple of this quantity, according to the number of analyses to be made, and after chroming and washing as directed, squeeze to a weight representing 70 to 75 per cent water. Weigh the whole amount and divide by the multiple of the grams of actual dry hide powder taken to obtain the weight of the wet hide powder for 200 cc of solution. *The hide powder should always be used the same day that it is washed.*

The nontannin filtrate must not give a precipitate with a 1 per cent gelatin, 10 per cent salt solution.

TANNIN.

The tannin content is shown by the difference between the soluble solids and the corrected nontannins.

ANALYTICAL RESULTS.

The results received from those cooperating are given in the following tables:

TABLE 1.—*The extraction of fat by petroleum ether.*

Analyst.	Address.	Sample No. 1.				Sample No. 2.			
		6 hours.	8 hours.	10 hours.	24 hours.	6 hours.	8 hours.	10 hours.	24 hours.
J. R. Blockey ¹	Leathersellers Co.'s Technical College, London.	2.07	2.10	2.05	2.16	28.80	29.00	29.30	29.40
		2.00	2.10	2.10	2.07	29.00	29.20	29.40	29.60
M. F. Nichols.....	Nichols's Laboratory, Grand Rapids, Mich.	2.04	2.09	2.08	2.09	29.33	29.10	29.72	29.74
		2.06	2.05	2.04	2.08	*30.00	29.30	*30.00	29.47
J. M. Seltzer.....	Kistler Lesh & Co., Lock Haven, Pa.	1.97	2.02	2.06	2.09	29.17	29.11	29.47	29.54
		1.95	2.00	1.98	2.07	29.13	29.13	29.35	29.40
J. S. Rogers.....	Bureau of Chemistry, Washington, D. C.	1.98	2.02	2.02	2.05	29.27	29.47	29.63	29.64
		1.97	1.98	2.04	2.06	29.39	29.63	29.67
B. J. Ray ²	Agricultural Experiment Station, Raleigh, N. C.	2.03	1.99	2.15	2.04	29.25	*25.19	29.41	29.47
		1.97	2.10	2.06	29.30
P. F. Trowbridge..	Agricultural Experiment Station, Columbia, Mo.	1.99	1.99	1.97	1.92	29.06	28.92	29.29	29.23
		2.17	1.90	1.99	1.99	28.78	*28.39	29.30	*28.92
T. A. Faust.....	Yocum-Eachus Laboratory, Newark, N. J.	2.01	2.12	2.02	*2.27	28.97	28.95	29.33	29.68
		2.07	2.17	2.19	*2.31	29.01	29.30	29.14	29.38
Averages.....		2.02	2.04	2.04	2.05	29.09	29.14	29.41	29.49

¹ The siphonings occurred from 6 to 8 times per hour.

² The result *25.19 is thought to be too low on account of the leather being too tightly packed in the extraction thimble.

NOTE.—Results marked with an asterisk are not included in the averages.

Average soluble solids.....	14.0	5.1			15.4	5.5	10.5	2.22	1.64	13.5	4.6			
Average nontannins.....														
Average tannins.....			8.3											
Average glucose (A).....			2.36										9.0	
Average glucose (B).....					1.53								2.02	
														1.41

¹ The sugar solutions for these determinations were cleared by normal lead acetate.

² The sugar solutions for these determinations were cleared by basic lead acetate.

³ The extracts used by Mr. Ray for sugar determinations stood about 2 weeks before being analyzed, and considerable fermentation had taken place, shown by growths on the surfaces of the solutions. This undoubtedly explains the results obtained.

⁴ Mr. Blockay converted the cuprous oxid in the sugar determination into cupric oxid and weighed in that form. He found that the results obtained by this method checked with those obtained by the prescribed method.

⁵ Sodium carbonate was used in excess instead of potassium oxalate for removing the lead.

NOTE.—Results marked with an asterisk are not included in the averages.

COMMENTS BY ANALYSTS.

B. J. RAY. (1) *Fat determination*.—Under the work of fats I have one suggestion which I believe very important. It seems to make a great deal of difference whether the material is placed in the thimble loosely or tightly. In one instance I packed the ground leather in the thimble just as tightly as I could and not split it, for our Soxhlets were rather small to hold the required 15 grams, and found to my surprise that eight hours' extraction, which I had previously found to be sufficient for the first leather, left over 4 per cent of fat behind. I then ran a series of extractions on this thimble with the results shown below. Thirty-eight hours were required to give complete extraction. So it seems to me that when work is being done on such a sample as this one, where the material may easily be packed too hard, it should be stated that the sample is to be loosely packed in the Soxhlet thimble. Where the leather was loosely packed eight hours gave complete extraction.

Time of extraction, hours:	Per cent.
8	25.19
10	29.09
12	29.16
14	29.21
16	29.25
18	29.28
20	29.30
22	29.32
24	29.34
32	29.40
38	29.43

Extraction of uncombined tannins and nontannins.—I must say that I like the alcohol method best. It is simpler, it does not require the transferring of the material from one vessel to another, and hence a chance of loss. It is shorter and easier.

Soluble solids.—Some of the solutions have stood for two weeks or more before they were used. Certain growths could be seen on the surface of the solutions. A glance at the results will show you that either the methods do not give the best results, or that some change takes place in the solutions on standing. I believe the latter. So I made up four solutions by the alcohol method on leather No. 1 and immediately determined soluble solids, after adding to Nos. 3 and 4 10 cc of chloroform. The results are shown in the following table:

Effect of standing on the determination of soluble solids.

Sample.	Soluble solids determined—		
	Immediately.	After 2 days.	After 6 days.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
1, no chloroform	26.57	26.18	25.53
2, no chloroform	25.17	25.00	23.52
3, 10 cc chloroform	25.60	25.31	25.28
4, 10 cc chloroform	25.51	25.27	25.00

[Mr. Ray calls attention to the fact that after 6 days' standing, in solutions No. 1 and No. 2, to which no chloroform was added, the per cent of soluble solids dropped 1.04 and 1.65 per cent, respectively, and in solutions No. 3 and 4, to which chloroform was added, the drop in soluble solids was only 0.32 and 0.51 per cent, respectively.]

I further suggest that in the evaporating of the filtrate in the determination of soluble solids, a beaker cover be used instead of a flat bottomed glass dish. Place the tared beaker covers on water bath and allow the clear solution to flow slowly in from a separatory funnel as the solution evaporates. Rinse out the funnel finally with a few cubic centimeters of distilled water. Dry in water oven to constant weight. Why dry for 12 hours? I found that in most cases only four hours were necessary for constant weight; some required six.

Glucose.—In case of sample No. 1, the results on sugar vary enormously, and I do not know how to account for this, since in two cases the duplicates agree fairly well; the other two are way off.

[Mr. Ray also states that he believes that the variations in his results on the determination of glucose are due to the long standing of the solutions before analysis. In this respect he is undoubtedly correct, for it is well known that fermentation will destroy the sugars.]

J. M. SELTZER. Fat determination.—The results of 6, 8, 10, and 24 hours' extraction are practically the same with leather No. 1, while with leather No. 2, 10 and 24 hours' extraction show slightly higher results over 6 and 8 hours' extraction.

Water-soluble matter.—In the Bureau of Chemistry method, when the water bath was kept at 50°, the solution in the extractor was heated to only 45°. This method shows higher results than the official A. L. C. A. method, and the resulting solution had a very much darker color, which was due to the boiling of it. I also extracted the two leathers by the A. L. C. A. method without removing the fat, and found that in sample No. 1 (following table) the results were almost the same as those in which the fat was first removed; but with No. 2 the results were very much lower by not removing the fat.

Data obtained when fat was not removed before extraction.

Method and sample.	Soluble solids.	Corrected nontannins.	Glucose A.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
Sample 1:			
A. L. C. A. method.....	23.22	12.75	8.28
Alcohol method.....	21.00	11.60	7.43
Sample 2:			
A. L. C. A. method.....	12.74	5.70	2.63

Alcohol extraction.—My results on the extraction with 95 per cent alcohol are contrary to those claimed for this method. Most of the sugar is removed by eight hours' extraction. The alcohol dissolves some matter which is insoluble in water after the alcohol is evaporated, as the water solution is very cloudy.

Sugar determination.—It has been shown before that basic lead acetate gives lower results than normal lead acetate, and my results also show the same to be true.

J. R. BLOCKEY. Fat determination.—The results show that by using the prescribed method of extraction very little is to be gained by prolonging the extraction over 10 hours. Experiments were made siphoning over at about 10 times per hour, and instead of using a thimble, the leather powder was very loosely packed in the Soxhlet, in the bottom of which was placed glass wool to prevent solid particles from siphoning over. It was found that 1½ hours were sufficient to extract 29.2 per cent of the fat from No. 2, or practically as much as is extracted in 10 hours, siphoning at the rate of four times an hour and using a thimble.

On the whole it seems preferable to extract by giving 12 to 15 siphonings, and if there is reason to suppose that all of the fat has not been extracted, to continue the extraction with a fresh flask. For instance, if there is reason to suspect the presence of castor oil, then petroleum ether will only slowly extract this, as the solubility of castor oil in petroleum ether is very low. By continuing the extraction with a fresh flask the castor oil would be detected.

The drying of the fat residue until constant in weight is not always easy, as with oxidizable oils especially oxidation may take place and thereby increase the weight, and volatilization may also take place, especially with mineral oils, and thereby decrease the weight. Perfect constancy is therefore not to be expected, and it scarcely seems fair to establish set rules and time for the extraction and drying of fatty matters, as the character of the oils and fats employed varies so much.

Water-soluble matter.—A. L. C. A. method (see p. 229). Procter's extractor was employed. No difficulty was experienced in the extraction, and the liquor was coming over colorless at the end. Nontannin experiments made with American chromed hide powder gave no appreciable difference from experiments with powder chromed according to the official I. A. L. T. C. method.¹

¹ Procter, Leather Industries: Laboratory Book on Analytical Experimental Methods, p. 212.

although washing of the powder chromed with chrome alum was more difficult than with chrome chlorid, the end point with barium chlorid being not so sensitive as the end point with silver nitrate and potassium chromate.

Alcohol method.—With regard to this method very much might be said in criticism. The first point to consider is, What do we wish to find out from the amount of soluble matter? Leather can not be considered as consisting of a definite chemical substance (composed of hide fiber and tannin) and a certain amount of excess of tan, nor can these two be quantitatively separated. There is no such sharp line of demarcation between the combined tannin and the uncombined tannin, for on washing leather there is practically no point at which the tannin ceases to be washed out. The best that can be done is an approximation, and this can be obtained quite well by the ordinary method of washing with water as exemplified in the prescribed A. L. C. A. method. For any method to supersede this method it should possess distinct advantage. One of the advantages claimed for the alcohol method over the ordinary method of extraction is that it is possible to differentiate between the natural soluble matters, such as tannins, and the artificial soluble matters, such as glucose and Epsom salts. It has been stated that 95 per cent alcohol does not dissolve glucose or Epsom salts, whereas actually it dissolves both, 95 per cent alcohol dissolving glucose to the extent of over 1 per cent. Since glucose is soluble in 95 per cent alcohol, though only to the extent of 1 per cent, the amount extracted in a Soxhlet apparatus may be noteworthy, considering the volume of alcohol which siphons through the apparatus in the course of the extraction. The results show that 6 per cent out of 8 per cent of the glucose is extracted in eight hours.

This should be sufficient to condemn the method, even if no further disadvantage could be charged against it. Another disadvantage is the increased number of operations involved and the extra time required. The evaporation of the alcohol on the steam bath is an unsatisfactory operation, as resinous substances separate out and oxidization may take place. Ninety-five per cent alcohol is expensive and according to the method can not be used over again. Moreover, if the leather is not perfectly dry before the extraction, the alcohol will no longer be 95 per cent after it has once come in contact with the leather.

The advantage claimed for this method over the water extraction method (i. e., that there is no need to estimate the mineral ash in the soluble matter as recommended by Parker and Paul) does not hold, because by both methods mineral matter is dissolved out in the extraction, so that both are liable to the same error unless the soluble mineral matter is estimated. Moreover, this determination is very easily and rapidly made.

Glucose.—The method as adopted was as prescribed, except after washing the cuprous oxid precipitate until free from alkali the crucible was removed and heated in the flame, gently at first to drive off the moisture, and strongly afterwards to convert the red cuprous oxid to black copper oxid. The crucible is allowed to cool in a desiccator and the residue weighed as cupric oxid (CuO). Preliminary experiments showed that the results were exactly the same, whether the residue was weighed as free copper or as cuprous oxid (Cu_2O) or as cupric oxid (CuO).

The precipitation of the excess of lead with solid potassium oxalate possesses one advantage over the ordinary method of using a strong solution of sodium sulphate, in that there is no dilution of the liquor, but it is doubtful if this advantage overbalances the disadvantage of the extra time taken in determining when all the lead has been removed. The same remark exactly applies to the neutralization of the hydrochloric acid by anhydrous sodium carbonate after inversion.

The ordinary method of neutralizing the acid by a known volume of strong caustic soda solution involves the dilution of the liquor and a further complication in the calculation, but it is quicker than the neutralization with the solid sodium carbonate. Experiments were performed, using the different methods, but the results showed no appreciable difference.

With regard to the difference between the use of normal and basic lead acetates it will be seen that the results in every case are higher with the normal than with the basic. It is impossible to say without a knowledge of the exact amount of glucose actually present in the leather which of the two gives the more correct results; that is, whether the figures obtained with the use of normal lead acetate are closer to the actual amount than with basic lead acetate.

Experiments were performed on solutions containing known quantities of glucose to determine, if possible, what the cause was of this higher result ob-

tained with normal lead acetate. The results of these experiments will be published in a short time. The higher results obtained with normal lead acetate are probably due to the presence of substances like gallic acid, which reduce Fehling solution and give a precipitate with lead acetate that is soluble in dilute acids such as acetic acid. By the use of basic lead acetate some of the free acid is probably neutralized, so that the precipitation of the gallic acid and kindred substances is more complete than with normal lead acetate.

Both are liable to the same sort of error, but the error in the case of the normal is higher than with the basic, so that it seems preferable to use the latter. In any case, it is essential that the glucose determination should be performed immediately after the soluble solid extraction has been made. If the soluble solid solution is allowed to stand, decomposition takes place, and very conflicting results were obtained when experiments were made on the solutions which had been standing. By using basic lead acetate on such a solution, the amount of glucose was very much reduced, whereas in one case by using normal lead acetate the amount was actually increased. This is probably due to decomposition into substances which are not entirely removed by normal acetate, and which reduce Fehling's solution. On the whole, the use of basic lead acetate is to be preferred to normal lead acetate.

T. A. FAUST. *Fat extraction*.—For extraction of grease from leather, I used a special apparatus having ground-glass joints and a Hopkins condenser, cork and rubber connections being unsatisfactory. In the case of both leathers the 24-hour extraction seemed to give abnormal results; and, in my opinion, the 8-hour extraction is sufficient for either sole, belting, or harness leather.

Extraction of uncombined tannins and nontannins (A. L. C. A. method).—Concordant results can be obtained by using this method, provided the temperature is always 50° and that absolutely the same temperature is kept during the extraction of different samples of leather. The method, however, is an empirical one, as a few degrees' difference in the temperature makes a considerable difference in the results. There is a constant breaking down of leather substance by the continued digestion with water even at this temperature, thus making the results depend entirely upon the temperature, time of extraction, and degree of tannage of the leather. The results by this method are not as concordant as those by the alcohol method.

Bureau of Chemistry method.—The apparatus as suggested in the Bureau of Chemistry method is rather cumbersome, and considerable difficulty in manipulation was experienced. Constant attention was required to prevent the temperature in the water jacket from getting above 50° , and it was very difficult to drive the steam through the water jacket at this temperature because the steam was condensed. It was almost 2 hours before the first siphoning took place. The result on leather No. 1 is lower than by either the alcohol or the A. L. C. A. method of extraction, and I believe it is due to the fact that the apparatus did not siphon often enough. I have no results on leather No. 2, as I was not favorably impressed with the method and did no more work with this apparatus.

Alcohol extraction.—This method seems to be very promising, as it is not empirical to the extent that the water extraction is, where no definite end point is reached, nor is there the breaking down of leather substance and dissociation of tannin that there is in the water extraction. The tannin extracted by alcohol is, I believe, actual uncombined tannin, which is more than I can say of the tannin extracted by water. An examination of the leather residues after extraction with water showed a more or less dissociated and jumbled mass of leather, whereas in the alcohol extraction the leather seemed to retain practically its original condition. It is true that Epsom salts are soluble in alcohol, but to a limited extent. I believe that this error can be ignored for commercial analyses.

Glucose, however, is quite soluble in alcohol, so that there is probably no advantage in the alcohol method in this respect.

Glucose.—I think that basic lead acetate gives too low results and consequently did not complete all determinations with this reagent. Sodium carbonate was used in this work instead of potassium oxalate, as two samples which I have tried with potassium oxalate ran 8.70 and 8.41 per cent of glucose, as against 7.27 and 7.52 per cent (as reported) using sodium carbonate. This led me to believe that the results with potassium oxalate were too high, and I fell back on the sodium carbonate, which I have always used in the past. I believe, however, that potassium oxalate, being a neutral salt, is preferable to sodium carbonate, as it is quite difficult to know just when enough sodium carbonate is added to precipitate all of the lead. In my first report I mentioned

the fact that difficulty was experienced in securing good duplicates, and I have no doubt by this time that this was caused by the fact that in adding an uneven amount of sodium carbonate in order to be certain of the removal of all lead, conditions of alkalinity were established in the filtrate which caused the poor duplicates. Excellent duplicates were secured on the actual precipitation of the glucose in the filtrate after inversion and neutralization, proving that the source of my trouble was not in the handling of the copper precipitate.

I think the method which you have outlined for the work on the subject this year is much better than the present method. I believe the refluxing to be a great improvement over the evaporating, and I also believe your proportion of lead acetate to the volume of solution to be better than that called for by the present method. Personally, I would prefer taking a little larger quantity of the solution, which would obviate the necessity of waiting so long for sufficient filtrate from which to remove the lead and yet have the 150 cc required for inversion. The determinations of glucose in water extract and alcohol extract were fairly concordant.

GENERAL SUMMARY BY REFEREE.

DETERMINATION OF FATS.

The results on the extraction of fats taken as a whole agree very well. In sample No. 1, which contained about 2 per cent fat, judging from the averages as shown in Table 1, all except 0.03 per cent of the fat was removed in 6 hours. In sample No. 2, containing from 29 to 30 per cent of fat, the averages indicate that 10 hours' extraction removes all but 0.08 per cent of the fat present. Table 1 shows that in the results obtained by the 24 hours' extraction both in samples No. 1 and No. 2 there are a few abnormally low results. These, I think, may be due (as suggested by Ray and Blockey) to the leather being packed too tightly in the extraction thimble. No mention was made of this precaution in the directions, because it was thought that the necessity of loosely packing the leather in the Soxhlet was self-evident. If the packing of the leather be carefully avoided and the siphonings regulated to approximately 10 per hour, I believe that 10 hours' extraction will be more than sufficient to completely remove the fat, even from a heavily greased leather, and that leathers containing a low percentage of fat can be extracted in from 6 to 8 hours.

EXTRACTION OF SOLUBLES.

After comparing the three methods of extraction, I give the Bureau of Chemistry method the preference. Some claim that this method is cumbersome and the apparatus difficult to arrange and manipulate. I have found no trouble in this direction; in fact, it requires only a small amount of ingenuity to arrange and manipulate the apparatus as described in the directions. Of course it is not expected that the side tube of the Soxhlet will pass through the water bath which surrounds the extractor and which is kept at 50° C. This tube must pass to the condenser outside of the bath or there will be a large amount of condensation and running back into the extraction flask and the extraction will progress very slowly. Although the total time required for the extraction is longer than that in either of the other methods, the time actually used in manipulation is but little more. The results for soluble solids and tannins are higher than by the A. L. C. A. method, while the nontannins remain practically the same. This indicates that while a small amount of tannin may be destroyed by boiling the extract, more of the uncombined tannin present is removed. The A. L. C. A. method undoubtedly removes practically all of the readily soluble tannins, but the more difficultly soluble tannins, such as the "reds," require much longer extraction, such as is given by the Bureau

of Chemistry method. Since the extracts obtained by this method, when tested for soluble hide, gave no indication of its presence, it is evident that practically no combined tannin was removed; and since the soluble solids obtained by the Bureau of Chemistry method are usually about the same or a little lower than those by the alcohol method, it seems that Mr. Faust's comment, that extraction by the Bureau of Chemistry method removes combined tannin and breaks up the leather, is not well-grounded. The A. L. C. A. method gives very satisfactory results, save for the fact that it does not remove the more difficultly soluble tannins.

The alcohol method, contrary to the claims of Riker, does remove nearly all of the sugar present. (See Table 2, Glucose B.) The extract, when evaporated with water, always becomes cloudy, and considerable gummy, resinous matter remains insoluble, making manipulation difficult. Sometimes it is nearly impossible to obtain a clear soluble solid filtrate. In my own experience, I have found the results by this method little higher than those of the Bureau of Chemistry method, and I do not find a sharper end point in the extraction. A leather residue, after being extracted with vigorously boiling 95 per cent alcohol for 8 hours, was washed once with water, and the washing water gave a heavy precipitate with a gelatin salt solution.

GLUCOSE.

A comparison of the results obtained for Glucose A (cleared with normal lead acetate) and Glucose B (cleared with basic lead acetate) is very interesting. Sample No. 1 (Table 2) was a specially prepared leather and contained a definitely known amount of glucose. The amount actually added was 7.73 per cent, and the blank on the original leather gave 0.60 per cent, making 8.33 per cent total sugar in the leather. It is evident from Table 2 that in every case where basic lead acetate was used as a clearing agent the percentage of sugar found was much lower than the percentage of sugar actually added. Furthermore, the average of all sugar determinations made on extracts obtained by the A. L. C. A. and the Bureau of Chemistry methods and cleared by normal lead acetate was 8.39 per cent, or within 0.06 per cent of the theoretical amount of sugar present. In sample No. 2 (Table 2) the results for Glucose A and Glucose B indicate that the same rule holds good. This shows clearly that theoretical results can be obtained with normal lead acetate and that the basic lead acetate removes sugar and invariably gives low results.

RECOMMENDATIONS.

It is recommended that the following methods for the analysis of leather be adopted as provisional methods:

1. PREPARATION OF SAMPLE.

Reduce the sample to state of fineness such that it will pass through a millimeter sieve (it must not contain hard lumps). Avoid all unnecessary heating during grinding. Spread the sample out and allow it to return to atmospheric moisture conditions, mix thoroughly, and place in a tightly covered container.

2. MOISTURE.

Weigh 10 grams of the prepared sample into a wide, shallow, covered weighing bottle (or a similar dish which may be covered tightly when it is removed from the drying oven), and dry for 15 hours in a water oven at from 98° to 100° C. Cover the weighing bottle when it is removed from the oven, desiccate over sulphuric acid, and weigh. If it is desired to determine the moisture originally present, the leather must be quickly cut in small pieces with a knife and dried in the usual way without grinding.

3. ASH.

Slowly incinerate 5 grams of the prepared sample at a dull-red heat. (In case difficulty is experienced in burning off the carbon, leach out the residue with hot water, filter on an ashless filter, dry and ignite the filter and residue, add the filtrate, evaporate to dryness, and ignite.) Desiccate over sulphuric acid and weigh.

4. FATS.

Place loosely 15 grams of the prepared leather in a Soxhlet extractor containing a layer of fat-free cotton and cover with another layer of cotton. Extract with petroleum ether, distilling between 50° and 80° C. for from 8 to 10 hours. Heavily greased leathers (containing 15 per cent or more) will require the maximum time. Regulate the boiling so as to give from 10 to 15 siphonings per hour. Remove the flask, evaporate the petroleum ether on a steam bath, and dry in a water oven at from 98° to 100° C. to practically constant weight. Desiccate and weigh. Retain the leather residue from the fat extraction for the extraction of water solubles.

5. EXTRACTION OF WATER SOLUBLES.

Thoroughly moisten the leather residue from the fat extraction. Transfer to a Soxhlet extractor designed for making extractions at low temperatures and containing a layer of cotton. Place cotton above the leather in the extractor to prevent it from being carried over at the time of siphoning and extract at 50° C. At the beginning of the extraction, pour 25 cc of distilled water (including that used in moistening the leather) into the Soxhlet and allow it to siphon into the flask below, then begin the boiling. At the end of the first hour, remove the flame and transfer the extract to a 1-liter graduated flask. Add 175 cc of distilled water to the Soxhlet and continue the extraction for 2 hours. Transfer the extract to the graduated flask, add 175 cc water, and extract for 3 hours. Transfer the extract to the graduated flask, add 175 cc water and extract for 4 hours. Transfer the last portion of the extract to the graduated flask. This gives 14 hours' extraction and an extract that does not exceed 1 liter in volume. Make the extract up to 1 liter at room temperature. A few drops of toluene or carbolic acid must be added to the leather extract to prevent the fermentation of sugars.

6. GLUCOSE.

(a) *Preparation of solution.*

To 200 cc of the leather extract add 25 cc of a saturated solution of normal lead acetate, mix thoroughly, allow to stand about 15 minutes, and filter. The funnels and beakers must be kept covered to prevent evaporation. Precipitate the lead from this filtrate with a slight excess of solid potassium oxalate and filter. Pipette 150 cc of the last filtrate into a 600 cc Erlenmeyer flask, add 5 cc of concentrated hydrochloric acid and boil under a reflux condenser for two hours. Cool, neutralize with anhydrous sodium carbonate (using phenolphthalein), transfer to a 200 cc graduated flask, and make to volume. Filter through a double filter. (This filtrate must be clear.)

(b) *Determination.*

Use 50 cc of this filtrate for the determination of sugar, following the method for determining sugars in general (Munson and Walker), Bulletin 107, Revised, pages 241-242.

7. TOTAL SOLIDS.

Thoroughly mix the original extract, immediately pipette 10 cc into a tared dish, evaporate, and dry as directed in "Methods for the analysis of tanning materials," Bulletin 107, Revised, page 37, under "4. Evaporation and drying."

8. SOLUBLE SOLIDS.

Determine as directed under "Methods for the analysis of tanning materials," Bulletin 107, Revised, page 36, "(c) Soluble solids."

9. NONTANNINS.

Prepare a quantity of hide powder sufficient for the number of analyses to be made *during one day only*, in the following manner: Digest with 10 times its weight of water until thoroughly soaked. Add 3 per cent of chrome alum in solution, agitate by either shaking or stirring occasionally for several hours, and let stand overnight. Wash by squeezing through linen, continuing the washing until the wash water gives no precipitate with barium chlorid. Squeeze the hide, using the press if necessary, so that the wet hide will contain between 70 and 75 per cent of water. Use approximately 20 grams of wet hide for moisture determination. Add to 200 cc of the original solution such a quantity of wet hide as will give the ratio of dry hide to tannin indicated by the following table:

Tannin range per 100 cc.	Dry hide powder per 200 cc.
0.35 to 0.45 gram-----	9 to 11 grams.
.25 to .35 gram-----	6.5 to 9 grams.
.18 to .28 gram-----	4 to 6.5 grams.
.00 to .15 gram-----	0 to 4 grams.

Add 2 grams of kaolin to the filtrate, stir, and filter through a folded filter S and S No. 590 of sufficient size to hold the whole filtrate, returning until clear. Evaporate 100 cc of the filtrate, dry, and weigh as directed under soluble solids. The weight of the residue must be corrected for the dilution caused by the water contained in the wet hide powder. (The nontannin filtrate must not give a precipitate with a 1 per cent gelatin, 10 per cent salt, solution.)

NOTE.—In order to limit the amount of air-dried powder used, determine the moisture in the air-dried hide powder and calculate the quantity equal to at least 15 grams of actual dry hide powder, take any multiple of this quantity, according to the number of analyses to be made, and after chroming and washing as directed, squeeze to a weight representing 70 to 75 per cent water. Weigh the whole amount and divide by the multiple of the grams of actual dry hide powder taken to obtain the weight of the wet hide powder for 200 cc of solution. *The hide powder should always be used the same day that it is washed.*

10. TANNIN.

The tannin content is shown by the difference between the soluble solids and the corrected nontannins.

11. NITROGEN.

Determine by the Kjeldahl or Gunning method, Bulletin 107, Revised, pages 5-7.

12. HIDE SUBSTANCE.

Multiply the percentage of nitrogen by 5.62 and the result will be the percentage of hide substance present.

It is further recommended that the work be continued, paying special attention to the development of tests indicative of the quality and durability of leather.

Mr. Mitchell, referee on food adulteration, moved that another associate refereeship on this subject be established to cover work on the determination of heavy metals in food products.

The motion was carried.

The remainder of the session was devoted to the work on drugs and medicinal plants, the following reports of referees and correlated papers being presented in abstract or by title.

REPORT ON MEDICINAL PLANTS AND DRUGS.

By L. F. KEBLER, *Referee*.

The work during the past year has been of singular interest in many ways, but the amount accomplished is not as much as desired, chiefly because of lack of available workers. The results again emphasize the great need of systematic study, sampling, analytical methods, and standards, both specific and applied, with a view to determining what degree of accuracy can be obtained by workers in the same and different laboratories.

The Pharmacopœia prescribes tests for all drugs recognized by this authority, including the source, analytical methods, standards, degree of purity, and limit of foreign matter, as the case may be. The subject of sampling is receiving careful consideration, and it is hoped that a full report with recommendations can be made at the next meeting. The source included in some of the tests is frequently of the utmost importance; for example, cardamon, "The dried, nearly ripe fruit of *Elettaria repens* (Sonnerat) Baillon (Fam. Zingiberacæ)." This standard clearly designates the source of the material, and if a sample should be found which is contaminated with bastard cardamon it is clearly evident that the article is not the article prescribed by the law. Many of the tests for crude drugs make no provision whatever for the presence of certain incidental or accidental foreign material that is usually present in these products.

Uva ursi has been offered for importation containing an excess of 40 per cent of stems, worthless leaves, and other foreign material. The excuse offered by the importer for the character of the drug was that it is intended for use in the manufacture of cattle powder or veterinary remedies. Steps have been taken to reduce the percentage of such material imported; in fact, certain imports have been permitted entry only on condition that the importer would eliminate the excessive amounts of foreign material.

An excellent example for this recommendation to be put into practice is in cubeb berries. There is no legal excuse for cubeb berries containing more than 5 per cent of foreign material, since, as commonly found in this commodity, it can be easily eliminated by mechanical means.

Experience has furthermore shown that it will be necessary to prohibit the importation of commodities containing excessive amounts of foreign material if the pharmaceutical and medical professions are to be supplied with agents suitable for treating the sick to the best advantage. It is hoped that prime goods will in time be offered free from impurities; in fact, the courts may make this necessary in order that the public may be protected. In the past certain goods have been released on the condition that they be marked indicating the nature and character of the impurities present. It subsequently developed that some of these goods were supplied on orders without indicating to the purchaser that the articles were not of proper quality. Such transactions at times result in the second dealer finding himself face to face with a violation of the law. Furthermore, such goods are at times shipped into interstate commerce with the correct marks, but after they have crossed the borders of the State the original package is broken and the consuming public is at the mercy of the dealers unless State officers interfere. It is hoped, therefore, that the officers charged with the supervision and enforcement of the State drug laws will take an active interest in these matters.

Some of the analytical methods did not give satisfactorily concordant results in the hands of different workers. For example, the method for determining the alkaloidal matter in *Hyoscyamus* is liable to a variation of 100 per cent when executed by experienced analysts, and naturally a method giving such

great variations as this would be difficult to employ to advantage for court work. The chief drawback with the method appears to be insufficient time and solvent to extract the alkaloids properly from the powdered drug.

Specific standards are prescribed in the tests for certain drugs. For example, the description of *Cannabis indica* states that the powder shall contain few or no stone cells, which means the virtual absence of seeds in the finished product. In practice it has been found exceedingly difficult to put such a standard in force and effect for the simple reason that there are few, if any, samples available on the market free from seeds to the extent prescribed. Furthermore, information is lacking as to just what amount of seed should or should not be permitted.

Attention is now called to standards that are indicated but not specifically set forth. Such standards include the amount of alcohol that should be present in finished products made according to certain prescribed formulas. For example, the Pharmacopœia gives a formula for manufacturing tincture of ginger, but no definite statement appears as to the amount of alcohol that should be present in the finished product, neither is there any reference as to the amount of nonvolatile matter that might possibly be present in a preparation made as directed by this authority. These features are most important, because it is well known that the alcoholic strength of the menstruum is quite different from the percentage of alcohol contained in the finished product. Ninety-five per cent alcohol usually extracts far less material than this solvent containing more water. This feature is taken advantage of by some manufacturers in preparing such articles as tincture of ginger or extract of ginger.

In a paper communicated to this association last year by Mr. Street on the subject of ginger extracts, attention was called to the fact that menstrea containing smaller amounts of alcohol than that contained in original (95 per cent) alcohol removed considerably more extractive matter than this 95 per cent alcohol. Your referee has conducted experiments on the same article with results that corroborate the findings of Mr. Street in this particular. The results will be communicated next year in a separate article entitled "Standard for tincture of ginger." The work was completed this year, but owing to other duties and absence from the city the results were not presented.

In this connection it might be well to call attention to the well-known fact that examinations and investigations of food and drug problems frequently overlap each other, and if it were possible to arrive at some plan whereby the efforts of investigators on subjects that have to a certain extent a common basis might be combined, it certainly would be most desirable. Such a plan would eliminate so-called double standards in many instances.

The associate referee on synthetic products, W. O. Emery, has conducted cooperative work during the past year and the report will be submitted.

H. C. Fuller has also conducted some cooperative work on medicated soft drinks and the report is presented.

Mr. Schneider has submitted a very voluminous paper on the subject of microscopical work, but the referee feels that a part of this paper does not deal specifically with the work assigned him as associate referee, and it is therefore suggested that only such parts of his report be considered as properly come within the scope of the work on medicinal plants.

Several papers on various subjects are presented. In some instances the results embodied in these papers involved cooperation, while others represent the work of a single individual.

In concluding, the referee feels that there has not been sufficient work done along the various lines to make definite recommendations, and for this reason

simply recommends that the work at present established be continued, with such modifications in the methods as the several associate referees have recommended.

REPORT ON HEADACHE MIXTURES.

By W. O. EMERY, *Associate Referee, Synthetic Drug Products.*

Cooperative work on headache preparations has been conducted during the past year according to the general plan put in operation four years ago and reported on at the last three meetings of the association. Two samples were submitted to cooperating chemists, one (No. 8) a powder mixture containing acetphenetidin, caffeine, and sodium bicarbonate; the other (No. 9) a liquid product consisting of alcohol, acetanilid, caffeine, sodium salicylate, water, glycerin, and oil of peppermint, of which constituents the first four named were to be estimated quantitatively. No. 8 was to be treated substantially in accordance with instructions outlined in Bulletin 132, page 198; for No. 9 the following directions were sent to the co-workers:

METHOD FOR ANALYZING LIQUID HEADACHE MIXTURE.¹

ALCOHOL.

Cool sample to 25° C., at which temperature fill a 25 cc flask² to mark, weigh, then transfer to a distilling apparatus,³ rinsing out the flask several times with water, employing for this purpose a total of 25 cc. Distil into a 50 cc flask (surrounded by ice water) until the liquid in the distilling flask is reduced to 10 cc. Transfer the somewhat turbid distillate (due to volatile oil) to a separator provided with short delivery tube, rinse out the flask several times with a total of 15 cc water, saturate the combined solution with sodium chlorid, shake vigorously for two minutes with 25 cc low boiling (40-60° C.) petroleum ether, then allow to stand 15 minutes. Draw off entire liquid into a second separator, washing out the first (which still contains undissolved salt) with 5 cc saturated salt solution into the second. Draw off the lower layer into first separator, from which the undissolved salt has in the meantime been removed, and shake it out as above with a second portion of 25 cc petroleum ether. Combine both ethereal extractions, wash with 25 cc saturated salt solution, draw off latter after 15 minutes and add to the distillate first treated, finally transferring resultant mixture to the distillation flask.⁴ Distil into a 50 cc flask (cooled in ice water) nearly to mark, allow temperature to rise to 25° C. fill to mark, and determine the specific gravity at this temperature in a Squibb pycnometer, calculating the per cent of alcohol by volume from tables in the United States Pharmacopœia, eighth revision. The percentage obtained multiplied by 2 will give the amount of alcohol in original sample.

CAFFEIN-ACETANILID.

Transfer residual crystalline magma containing the caffeine, acetanilid, and sodium salicylate from distilling flask to a separatory funnel by the aid of successive portions of water (ending with a little chloroform if necessary to remove all traces of acetanilid) so that the final volume of the aqueous solution

¹ Sample was prepared at the temperature of 25° C. in a flask graduated at 20° C. since it was found that at the latter temperature the acetanilid tended to separate in part from the solution.

² Only flasks graduated at 20° C. should be employed in determining the alcohol, during manipulation with the sample in hand, for reasons which are apparent after a consideration of the footnote above.

³ The apparatus consists of a half-liter, round-bottom flask standing on a perforated (1-inch) asbestos plate, so that the flame may never come in actual contact with any portion of the glass not covered by the liquid contents. In this way overheating may easily be avoided. The connection between flask and condenser is effected by means of tightly fitting rubber stoppers and doubly bent tube. The lower end of condenser is contracted sufficiently to permit entrance into neck of receiving flask immersed in ice water, thus avoiding use of adapter.

⁴ This method for the removal of volatile oils is substantially the same as that suggested by Thorpe and Holmes, *J. Chem. Soc.*, 1903, 83: 314.

does not exceed 50 cc. Make five separate extractions by means of vigorous shaking, each time with 70 cc chloroform. Allow solvent to clear after each extraction, pass through small (5.5 cc) dry filter into a 200 cc Erlenmeyer and distil by the aid of a small flame until about 60 cc have gone over. Use this distillate for each subsequent extraction, making up to 70 cc as found necessary with fresh solvent. After the final extraction and distillation of chloroform, add 10 cc dilute sulphuric acid and evaporate to 4 or 5 cc on steam bath; transfer the residual acid solution of caffein and anilin sulphate to a 100 cc graduated flask, fill to mark and determine caffein and acetanilid in an aliquot of 25 cc, as directed in method previously submitted. (See Bul. 132, p. 197.)

SODIUM SALICYLATE (SALICYLIC ACID).

The aqueous solution remaining in separatory funnel and containing the sodium salicylate and glycerin is rendered acid with hydrochloric acid and extracted three separate times by means of vigorous shaking, 70 cc chloroform being employed for each extraction. The solvent, after clearing, is run into a 200 cc erlenmeyer (containing 10 cc water and 1 gram dry sodium carbonate, sufficient to fix all the salicylic acid present) and distilled over a small flame until most of the chloroform has been expelled. After the final distillation and elimination of all chloroform, transfer the aqueous soda solution of sodium salicylate to a liter flask, add 10 grams dry sodium carbonate, fill to mark, pipette an aliquot of 100 cc into a 200 cc erlenmeyer, heat nearly to boiling, then add about 35 cc fifth normal iodine in potassium iodid (or double this quantity of tenth normal iodine solution), enough to insure an excess of iodine. Heat one hour on steam bath to near the boiling temperature, during which time a violet-red precipitate of tetraiodophenylquinone ($C_6H_2I_4O$)₂ will appear. Remove excess of iodine by the addition of a few drops of hypo solution, decant liquid off into a tared Gooch crucible, care being taken that most of the precipitate remains in the flask. Add 50 cc boiling water to the iodine compound in flask, digest for 10 minutes on steam bath, then pour into the gooch, in'to which the precipitate is gradually washed by means of hot water, using for this purpose about 200 cc. Dry to constant weight in air bath at 100° C. Multiply weight of precipitate by 0.4658 and the product will be the weight of sodium salicylate in aliquot taken. Report all results in parts per 100.

ANALYTICAL DATA.

The results obtained and reported have been tabulated as follows:

Cooperative results on headache mixtures.

[Percentage data.]

Analyst.	No. 8.				No. 9.			
	Chloroform-insoluble residue.	Caffeine.	Acetanilid.	Total.	Alcohol.	Caffeine.	Acetanilid.	Sodium salicylate.
J. M. Bartlett, Grono, Me.....	20.66 19.63	12.30 13.30 13.50 13.00	64.50 67.60 66.10	199.30	29.50	0.47	3.38	5.20
W. O. Emery, Washington, D. C.	21.10	13.12	65.67	99.89	29.34 29.50	.44 .44	3.49 3.48	5.22 5.21
Chas. W. Johnson, Seattle, Wash. ²	20.88 20.92	12.61 11.91	66.59 66.27	100.08 99.10	29.36	.45	3.48	5.26
C. C. Le Febvre, Washington, D. C.....	20.92 20.96	13.17 13.46	66.27 65.56	100.36 99.98	29.50	.43	3.46	5.16 5.17
H. M. Loomis, Seattle, Wash....	³ 21.78 ³ 21.19	13.02 13.62	66.76 66.84	101.56 101.65	29.26	.48 .48	3.38 3.38	5.12 5.15
C. B. Morrison, New Haven, Conn. ⁴	³ 20.86	13.30 13.30	66.60 66.30	100.76	29.67 29.50	.44	3.51	5.26

¹ Total of averages.

² No. 8 done by Josephine Johnson. No. 9 by J. J. Wier.

³ Result of titration.

⁴ Reported by J. P. Street.

Cooperative results on headache mixtures—Continued.

Analyst.	No. 8.				No. 9.			
	Chloroform-insoluble residue.	Caffeine.	Acetphenetidin.	Total.	Alcohol.	Caffeine.	Acetanilid.	Sodium salicylate.
R. R. Shively, Washington, D. C.	20.71	13.52	65.61	99.84	29.00	0.45	3.48	5.31
	21.07	13.24	65.73	100.04		.46		5.29
H. L. Schultz, Detroit, Mich.	20.70	12.85	66.40	99.95		.48	3.44	5.20
	20.80	12.30	66.30	99.40		.47	3.44	5.29
	20.66	13.40	65.60	99.66				
Average.....	20.86	13.08	66.16	100.11	29.40	.46	3.45	5.22
Maximum.....	21.78	13.80	67.60	29.67	.48	3.49	5.31
Minimum.....	19.63	11.91	64.50	29.00	.43	3.38	5.12
Difference.....	2.15	1.89	3.1067	.05	.11	.19
Known composition ¹	20.83	12.50	66.67	30.00	.45	3.56	5.36

¹ No. 8 prepared by mixing in mortar and repeated sifting of the air-dried ingredients in the proportion of: Acetphenetidin 89, sodium bicarbonate 25, caffeine 15. No. 9 prepared by dissolving acetanilid 70.1 grams, caffeine 8.78 grams, sodium salicylate 105.15 grams, oil peppermint 20 drops, glycerin 10 cc in 526.3 cc alcohol (95 per cent), and sufficient water to make 2 liters at 25° C. Such a mixture was calculated to yield a preparation containing alcohol 30 per cent, and acetanilid 16 grains, caffeine 2 grains, sodium salicylate 24 grains per fluid ounce.

DISCUSSION OF RESULTS.

Mr. Le Febvre reports observing on various occasions a whitish crystalline sublimation on the sides of dish used in heating the acetphenetidin residue at the full temperature of steam bath, in order to expel any excess of acetic anhydrid. This behavior indicates volatility of the former substance when heated unduly or for a long period, and probably explains the low values obtained by used a larger (300 cc) flask in his operations.

Mr. Loomis finds great difficulty in distilling chloroform from a 100 cc Erlenmeyer as specified in the directions, since it tends to suddenly boil up violently, some of the solution passing over into the condenser tube. He accordingly used a larger (300 cc) flask in his operations.

Mr. Street reports, in connection with the determination of sodium salicylate, that in an experiment with 0.1000 gram pure salicylic acid he obtained 0.2500 gram of the red iodine compound, or, using the factor 0.4012, an equivalent of 0.1003 gram of salicylic acid.

The tabulated results on No. 8 show a considerable range of variation, sufficient, in fact, to warrant further investigation with the same or a similar combination. These variations are due in part, doubtless, to inexperience; partly, also, to imperfections in the method itself, the exact nature of which does not at this time appear entirely clear. It has been known for some time that acetanilid, when heated above 40° C. in the dry state, suffers appreciable loss through sublimation; accordingly, it was found advantageous in estimating this substance to adopt a volumetric method. On the other hand, it was believed until quite recently that acetphenetidin could be heated for a long time at the ordinary temperature of the steam or vapor bath without material loss. It appears, however, that greater care will have to be exercised in all operations calculated to free acetphenetidin from the last traces of acetic acid and anhydrid. Aside from the apparent necessity of avoiding any undue excess of the anhydrid used in the acetylating process, it is suggested that only moderate heat be applied after each addition of the chloroform-alcohol mixture. Thus,

after expelling the major portion of acetic anhydrid on a moderately heated steam or vapor bath, the last traces will be more safely removed by permitting the evaporating dish to stand 24 to 48 hours in the open prior to weighing, or until repeated weighings indicate no further loss.

The objection to the employment of a 100-cc Erlenmeyer for the distillation of chloroform containing a dissolved substance as caffein or acetanilid is undoubtedly well taken, though any violent ebullition experienced by Mr. Loomis, and possibly, also, by others, can usually be avoided by gentle heat together with the presence of one or more glass beads in the distillation flask. However, a larger flask presents decided advantages, in that the rather numerous distillations required can be effected with greater expedition and without fear that any of the dissolved substances may be carried over mechanically with the chloroform vapor. At present a 200-cc Erlenmeyer is used in the Bureau of Chemistry, in connection with a spray trap substantially like the accompanying illustration (fig. 3).

A further change in the procedure outlined under caffein has been found advantageous. Instead of two extractions with chloroform of 80 cc each, we have gone over definitely to the alternative of three extractions of 60 cc solvent, substantially as given in footnote (c), page 197, Bulletin 132. Suitable recommendations covering the points involved have been presented to the association.

The values obtained on No. 9 are reasonably close in agreement, particularly so in the case of alcohol, when one considers the

opportunity for loss presented in the operation to eliminate essential oil from the alcoholic distillate. The flask and condenser used in determining the alcohol are shown in their relative dimensions in figure 4.

During the course of our investigations of headache and other medicinal preparations new problems constantly arise, involving, in whole or part, the methods already presented to this association. More frequently, however, it is found necessary to modify or amplify these methods so as to fit the particular combination under investigation. Two such problems I desire to bring to your attention at this time, namely, the treatment of mixtures containing, on the one hand, codein, caffein, and acetphenetidin; on the other, antipyrin and acetanilid. The method followed in the first case is substantially as follows:

CODEIN, CAFFEIN, AND ACETPHENETIDIN MIXTURE.

Codein.

Weigh out about 0.3500 grams of powdered material (if in pill or tablet form at least 10 of these should be reduced to powder), transfer to a separatory

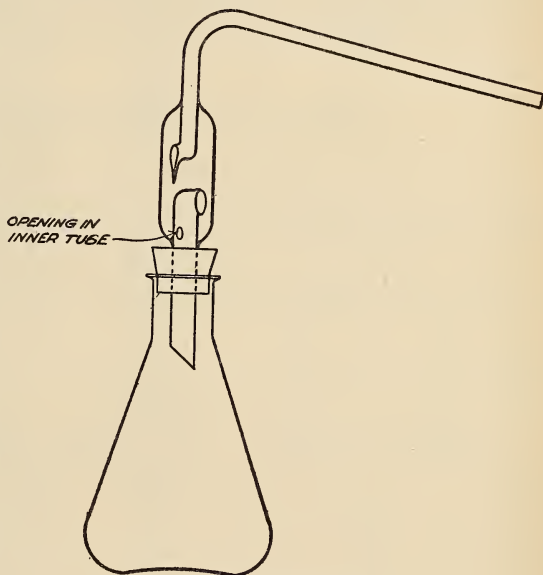


FIG. 3.—Spray trap.

funnel by means of 10 cc very dilute sulphuric acid (or sufficient to render the solution decidedly acid after neutralization of any carbonate that may be present), extract by means of vigorous shaking with 50 cc of chloroform. After clearing draw off the solvent, allowing it to run through a small (5.5 cm) filter into a 200 cc erlenmeyer. Distil off about 50 cc chloroform, using a small Bunsen flame. Extract a second and third time with same amount of solvent as first used. Allow the chloroform from each extraction to run into the erlenmeyer, then distil off all but about 10 cc. Now add 10 cc dilute sulphuric acid (1 volume concentrated acid to 5 of water) and heat on steam bath until the chloroform has disappeared and only about 5 cc of the acid liquid remains, then treat as directed under caffeine.

Render the acid liquid in separator containing the codein sulphate neutral by the addition of solid sodium bicarbonate, wash out filter used in the preceding operation to clarify the chloroform, once with water, allowing latter to run into the separator, then reextract three separate times with 50 cc chloroform. Collect solvent as above directed in a second 200 cc erlenmeyer, distilling off most of the liquid by the aid of gentle heat. Transfer residual chloroform to a small beaker or evaporating dish, using sufficient fresh chloroform for this purpose. heat gently over steam bath to dryness, cool, and weigh as anhydrous codein.

Caffein and acetphenetidin.

The aqueous acid solution containing the caffein and phenetidin sulphate is transferred to a separatory funnel and treated substantially as directed under the respective headings on page 198, Bulletin 132.

The procedure covering the second case is as follows:

ANTIPIRYN AND ACETANILID MIXTURE.

Antipyrin.

If in powder form (pills and tablets should naturally be reduced to such condition), weigh out 0.2 to 0.4 gram in a 50 cc erlenmeyer, add 10 cc dilute sulphuric acid (1 volume concentrated acid to 5 of water) and heat on steam bath till the residual liquid amounts to about 5 cc. Pour and rinse into a separatory funnel so that final volume does not exceed 20 cc. Extract 5 times with chloroform, using 50 cc for each extraction. Pass the solvent through a small (5.5 cm) dry filter into a 200 cc erlenmeyer and distil over a small flame down to about 10 cc. Transfer the combined residue obtained after the fifth extraction by means of small quantities of chloroform to a small tared beaker or crystallizing dish, evaporate solvent at moderate heat and at the ordinary temperature, dry the residual antipyrin in desiccator to constant weight.

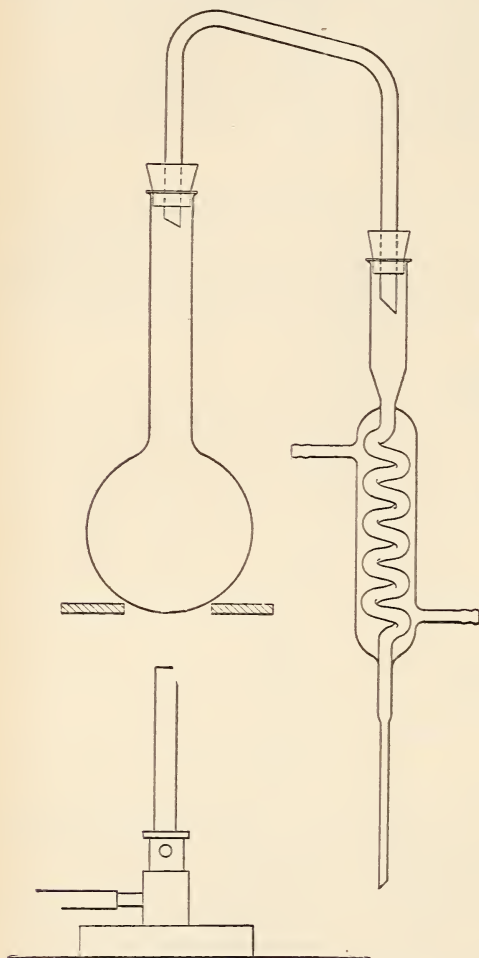


FIG. 4.—Alcohol distillation apparatus.

Acetanilid.

Transfer the acid solution remaining in separator and containing the anilin sulphate to a 100 cc erlenmeyer, heat on steam bath to expel traces of chloroform. Wash out the filter used in the preceding operation to clarify the solvent, once with water, allowing the latter to run into solution of anilin sulphate. Add 10 cc concentrated hydrochloric acid, a like amount of water, titrate with a standard solution of potassium bromid-bromate, then proceed substantially as directed on page 193 under the respective heading in Bulletin 132.

In the event that the mixture of acetanilid and antipyrin contains in addition caffeine, sodium bicarbonate, starch, or sugar, a powdered sample should be weighed out on a tared filter and chloroform used to separate the first three mentioned ingredients. After treating such a mixture of acetanilid, antipyrin, caffeine, etc., with dilute sulphuric acid on steam bath and subsequently with chloroform, the antipyrin and caffeine would be obtained together and can later be separated by means of mercuric nitrate.

Mixtures of antipyrin and acetphenetidin are treated in a manner similar to that for the separation of antipyrin and acetanilid up to the point of obtaining phenetidin sulphate. The acetphenetidin is then regenerated and weighed as such, according to directions given for the analysis of acetphenetidin headache mixtures.

REPORT ON MEDICATED SOFT DRINKS.

By H. C. FULLER, *Associate Referee.*

Ten collaborators reported results on the determination of solids, caffeine, cocain, and phosphoric acid in a soft-drink sample, using the methods as given in Bulletin 137, page 190, or Circular 66, page 7.

The results were obtained on a mixture prepared according to the following formula:

	Grams.
Water	10, 000
Sugar	10, 000
Caffein	50
	cc.
Fluid extract coca	200
Phosphoric acid	100
Lime juice	100
Caramel	100
Flavoring, consisting of the following	200
Oil of coriander	8
Oil nutmeg	15
Oil cassia	30
Alcohol	200

33547°—Bull. 152—12—16

The following results were reported:

Results reported by collaborating chemists.

Analyst.	Solids.	Caffein.	Cocain.	Phosphoric acid.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
M. C. Albrech, Pittsburgh, Pa.....	48.08	0.23	0.002	0.53
Edmund Clark, Boston, Mass.....	44.30	.20	.002	.45
E. O. Eaton, Washington, D. C.....	44.7748
W. O. Emery, Washington, D. C.....	54.1	.23	.002	.53
D. F. Fisher, Philadelphia, Pa.....	51.36	.29	.0012
H. C. Fuller, Washington, D. C.....	52.43	.23	.005	.49
	55.4	.22	.002	.53
2251
C. H. Kimberly, Philadelphia, Pa.....	44.4	.21	.004	.53
	48.4647
	50.5249
	50.09
C. B. Morrison, New Haven, Conn.....	53.12	.23	1 Positive.	.54
	53.05	.2454
E. K. Nelson, Washington, D. C.....	51.01	.22	.0013	.53
2253
A. E. Paul, Chicago, Ill.....21	.002(?)	.56
	52.7	.23	.0011	.53
A. Seidell, Washington, D. C.....	52.4
	49.0
	49.9

14. 4 mg found.

[As will be seen, with the exception of Emery's figures, the results obtained in the determination of caffeine agree very well, and those for phosphoric acid are also fairly concordant. The results for cocain show that it is doubtful if the small quantity present can be determined with absolute accuracy, though in proportion to the whole mixture the results obtained are fair. The method for determining total solids evidently needs revision, and the consensus of opinion was that 10 grams are sufficient for a sample instead of 25 cc as recommended in the method, and the residue should not be heated above 100° C. It is suggested that this work be continued during the ensuing year.]

ESTIMATING SMALL QUANTITIES OF MORPHIN IN MIXTURES.

By E. O. EATON.

At the last meeting the writer reported (Bul. 137, p. 188) a method for estimating small quantities of morphin in mixtures. During the past year this method was tried on the following samples:

Powdered opium: 10.77 per cent morphin U. S. P. assay.

Paregoric: U. S. P. preparations made up with 9 grams (10.77 per cent U. S. P. assay) opium to 2 liters; 100 cc=48.46 mg morphin.

Special sirup.

Sirup (U. S. P.) (cc)-----	1,000
Glycerin (cc)-----	100
Alcohol (cc)-----	100
Morphin hydrochlorid (grams)-----	1.03
Sodium bicarbonate (grams)-----	0.10
Oils of anise and peppermint, equal parts (cc)-----	0.5
Water sufficient to make (cc)-----	2,000
100 cc=43.58 mg morphin.	

RESULTS OBTAINED.

Powdered opium.

	Per cent.
E. O. Eaton-----	11
H. A. Seil-----	12.3
A. E. Stevenson-----	{ 9.96
	{ 9.72
	{ 10.02
H. E. Buchbinder-----	10.80

Paregoric.

	Mg per 100 cc.
E. O. Eaton-----	48.00
H. A. Seil-----	51.10
A. E. Stevenson-----	{ 36.00
	{ 30.90
H. E. Buchbinder-----	49.20

Special sirup.

	Mg per 100 cc.
E. O. Eaton-----	39.7
H. A. Seil-----	38.5
A. E. Stevenson-----	{ 28.8
	{ 30.9
H. E. Buchbinder-----	37.8

Three workers obtained fairly satisfactory results in the case of the paregoric and the special sirup. Stevenson's results plainly show difficulty somewhere. The results on opium are unsatisfactory. The reasons for the discrepancies in the latter are not plainly evident.

COMMENTS BY ANALYSTS.

H. A. Seil: On acetylating the residue obtained from the powdered opium and determining the morphin, 11.21 per cent was obtained.

A. E. Stevenson: In the assay of opium it required about seven washings to completely remove the uncombined alkaloids from the lime water solution. In both the paregoric and the opium it was found that about 50 per cent more alcohol-chloroform mixture than directed was required to extract the morphin. In each case the final residue was gummy and quite dark in color; it was difficult to dissolve in the fiftieth-normal acid and gave solutions of such color that the titration was finished with difficulty.

H. E. Buchbinder: I found from numerous experiments that the number of shake outs prescribed both in the first stage when the lime water is shaken out and later when the morphin is extracted is seldom sufficient. Would recommend:

1. That in both stages a minimum of seven extractions be made and that a small part of the last shake out be tested for alkaloids. If a reaction results the extraction is to be continued until a negative test is obtained.

2. If the alcohol-chloroform shake out is anything but a very light yellow it should be washed with small portions of water and the water in turn washed with suitable quantities of alcohol-chloroform, the latter to be added to the main alcohol-chloroform solution.

3. In place of cochineal as indicated use methyl red (three drops) as indicator; the change in color is very sharp and is only slightly affected by coloring matter. Moderate dilution does not affect the end point to the same extent as when cochineal is used.

4. Before adding standard acid dissolve in about 5 cc of warm neutral alcohol.

RECOMMENDATIONS.

It is recommended that the method as modified below be tried during the coming year. On page 189 of Bulletin 137, line 13, of method for opium, insert, "be sure to extract all of the morphin, using more shake outs, with alcohol and choloroform if necessary." Line 15, strike out word "tared" before "beaker" and "150 cc capacity" after beaker.

STANDARD FOR TINCTURE OF GINGER.

By L. F. KEBLER and C. H. KIMBERLY.

The United States Pharmacopœia, eighth revision, gives a method for making tincture of ginger, but does not prescribe a definite standard for the finished product. Since all commercial varieties are derived from the same species and the variation in quality is due entirely to different conditions of climate, soil, cultivation, etc., the Pharmacopœia places no restrictions whatsoever upon ginger when it says that ginger is the rhizome of *Zingiber officinalis* (Roscoe), and it is construed to mean that any available ginger may be employed in preparing the tincture. It is well known that the various gingers differ materially in aroma and pungency. These points are, however, not considered in this study.

PRELIMINARY EXAMINATIONS.

The names "tincture of ginger" and "extract of ginger" are frequently used interchangeably. An examination of a number of these products available on the market gave the following results:

Analytical data on ginger extracts and tinctures.

No.	Alcohol.	Residue.	Ash.	Capsicum.	Artificially colored.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>		
1	5.53	1.27	0.23	Present...	Yes.
2	56.76	.70	.15	...do.....	No.
3	87.00	2.86	.095	...do.....	Yes.
4	90.00	1.22	1.021	None.....	No.
5	10.00	5.40	.048	Trace.....	Yes.
6	24.00	3.30	.009	None.....	Yes.
7	70.80	3.84	.009	None.....	No.

The alcohol was determined by three methods, as follows:

(1) Dilute to three times the original volume and distil two volumes; determine specific gravity at 25° C. (2) Dilute to three volumes with saturated salt solution, shake out with petroleic ether, boiling point not above 60° C., discard the petroleic ether and distil two volumes; determine specific gravity at 25° C. (3) Add 10 cc of water and distil carefully to original volume. Method 2 is by far the best.

In some instances it was clearly indicated that the product was intended for medicinal purposes, but it was rarely stated that the article deviated from one prepared by the Pharmacopœial process. The results also show that a number of the preparations contain capsicum and are artificially colored. The amount of alcohol contained in Nos. 3 and 4 indicated that these samples were made with alcohol of proper strength and in accordance with the Pharmacopœial process, but the large amount of nonvolatile matter in No. 3 and the high

per cent of ash in No. 4, together with the fact that No. 3 was artificially colored and contained capsicum raised the question as to a specific standard for judging the quality of tincture of ginger. Apparently other workers have been in doubt as to constants for extract and tincture of ginger. Their work deals, however, more with ginger extract.¹

A number of samples of the tincture, representing the most prominent manufacturers, were then purchased and examined. There were also prepared in the laboratory according to the Pharmacopœial process two samples of tincture, one made with African ginger (No. 8) and the other with Jamaica ginger (No. 7). An examination of these samples gave the following results:

Examination of commercial and laboratory tinctures of ginger.

No.	Specific gravity at 25° C.	Alcohol claimed.	Alcohol found.	Non-volatile matter.	Ash.
		<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
1	0.8220	94	90	1.26	0.0075
2	.8201	90	90	1.12	.0066
3	.8144	95	91	1.25	.0068
4	.8184	88	90	1.60	.0074
5	.8271	91.2	87	1.27	.0049
6	.8210	89	89.5	1.59	.0145
7	.8140	U. S. P.	92	1.28	.0069
8	.8142	U. S. P.	90.5	1.36	.0062

¹ Made in laboratory.

COLLECTION OF POWDERED GINGER SAMPLES AND DETERMINATION OF DEGREE OF FINENESS.

The results obtained were still considered too meager to warrant the deduction of any definite standards for tincture of ginger. Arrangements were then made to procure samples of powdered ginger prepared from the various commercial varieties. As far as it was possible a sample of the whole rhizome from which the powdered gingers were prepared was also obtained. The uses to which ginger is put seem to demand different degrees of fineness; the condimental ginger being ground comparatively fine, while that used for Pharmacopœial purposes is usually coarsely ground, in fact, much coarser than is prescribed by the United States Pharmacopœia, eighth edition, which calls for a No. 50 powder. The degrees of fineness to which the samples obtained were ground were claimed to give the greatest satisfaction to drug firms who used them. Samples of the following varieties of ginger rhizome together with the powdered ginger or the ground ginger prepared therefrom were procured:

1. *African ginger*.—Unpeeled; dark brown color; fracture discolored in spots; odor good; taste sharp and pungent; rhizome small but of fair quality; the powder darker, finer, and more fibrous than sample No. 5, but lighter and coarser than No. 2.

2. *Jamaica ginger*.—Peeled, washed, and well dried; light yellow in color; brittle mealy fracture; odor slightly starchy; taste pungent. Powder derived from the above is quite fibrous, light colored, aromatic, and pungent.

3. *Cochin ginger*.—Unpeeled, dark, earthy appearing, with some soil attached, some rhizomes brittle, others tough; odor and taste correct; fiber showing in fracture. Powdered sample from above presents a very good appearance with but little fiber showing; color straw amber; quite finely ground; odor and taste good.

4. *Jamaica ginger*.—Peeled rhizomes larger and darker colored than Jamaica No. 2; apparently but little washed; very brittle in fracture; quite mealy;

¹ Street and Morrison, U. S. Dept. Agr., Bureau of Chemistry Bul. 137, p. 76; Lythgoe and Nurenberg, J. Ind. Eng. Chem., 1911, 3: 910.

odor cereal-like or starchy; taste aromatic and pungent; powder light in color, finely ground; color, odor, and taste good.

5. *African ginger*.—Unpeeled; very dark; roughly wrinkled, and rhizomes bony and coarse; fracture brittle, mealy; odor strong; usual pungent taste. Powder medium fine; color brown, not different from usual.

6. *Jamaica ginger*.—Peeled, washed; very light yellow; quite large rhizomes; odor like cereal; taste normal; finely ground; taste, color, and odor normal.

7. *Calcutta ginger*.—Very coarse; dark brown; almost black in places where cortex had been removed. Internally light brownish yellow; brittle; mealy, and showing bundles of fiber; odor and taste natural but weak. Ground sample quite dark and coarse, odor and taste normal.

8. *Calcutta ginger*.—Coarse; unpeeled; dirty, and more or less wormy; dark grayish brown. Sample powdered produced a dark powder quite finely ground, showing few fibers.

9 and 10. *Cochin ginger*.—Large; partially peeled rhizomes; very light yellow; some pieces darker; fracture brittle; odor and taste strong but natural. (9) Ground; represents practically No. 20 powder, being granulated about the size of ground coffee. This sample was also screened during grinding in order to remove dust and dirt; (10) finely ground for condiment purposes; light color; some fiber showing, odor and taste normal.

11 and 12. *African ginger*.—Dark brown, but lighter than African No. 1; unpeeled, except in spots; fracture brittle; odor and taste normal. (11) Ground to No. 20 fineness with its characteristics; (12) finely ground; brownish; dry; odor and taste acrid pungent.

13 and 14. *Japanese ginger*.—Decorticated; washed and lined, but not heavily; rhizome small; odor good, aromatic. (13) Coarsely ground, No. 20. (14) Finely ground; trifle darker than Jamaica, less fiber; odor and taste normal.

15 and 16. *Jamaica ginger*.—Peeled, washed, very light in color; small rhizome; odor and taste normal but strong; some dark rhizomes; fracture brittle; fibrous; odor and taste good. (15) Ground coarse, No. 20; (16) finely ground, showing less fiber; color light yellow; odor and taste normal.

17 and 18. *Calcutta ginger*.—Dark color; cortex coarse, thick; some soil attached. (17) Ground about No. 20, and screened during grinding; (18) ground very fine for condimental purposes, not screened. All samples ground to No. 20 were screened in grinding so that some of the earthy matter was removed. The more finely ground samples were not screened.

In order to determine the degree of fineness, samples were sifted through wire mesh sieves of standard size, using 150 grams in each case with the following results:

Determination of degree of fineness, using 150-gram samples.

No.	50 mesh.	40 mesh.	30 mesh.	20 mesh.	10 mesh.	Residue.	Remarks.
	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	
1.....	52	52	35	11	Fibrous.
2.....	30	31	27	31	30	Fibrous.
3.....	23	36	35	27	29	Fibrous.
4.....	52	52	35	11	
5.....	82	32	26	10	
6.....	71	21	25	24	9	Few fibers.
7.....	45	22	30	53	Trace.	Trace fiber.
8.....	112	38	Very finely ground.
9 ¹	12	45	30	63	
10 ²	30	120	Trace.	

¹ Nos. 11, 13, 15, and 17 were ground and sieved in same manner as No. 9.

² Nos. 12, 14, 16, and 18 were ground in same manner as No. 10.

These results clearly show that there is little powdered ginger supplied which complies with the degree of fineness prescribed by the Pharmacopœia (No. 50). What bearing this may have upon the finished product will be considered in connection with the results obtained in the examination of the tinctures made from the various samples.

EXAMINATION OF POWDERED SAMPLES.

In order to determine whether or not the samples complied in quality with the standards set for ginger by the committee on food standards (U. S. Dept. Agr., Office of Secretary, Cir. 19), it was decided to examine each sample by the official methods published in Bulletin 107, Revised. Wherever deviations from these methods were made, the fact is clearly indicated. A convenient quantity in the condition in which it was obtained was burned free from carbon, using as low a temperature as possible. The ash was boiled with 25 cc of 10 per cent hydrochloric acid, specific gravity 1.050, for five minutes, the insoluble material was collected in a Gooch crucible, washed with hot water, ignited, and weighed. The iron and aluminum were precipitated by ammonium hydroxid, and the quantity merely noted by comparison. The filtrate left after removing the above was heated to 50° C., rendered acid, if not acid, with acetic acid, and ammonium oxalate added. The calcium oxalate was filtered, washed, ignited, and then blasted to convert it into calcium oxid, and weighed.

The cold water extractive was determined by placing 4 grams in a 200 cc flask; water added to the mark, shaken at intervals of half an hour during eight hours' time, and allowed to stand 16 hours without shaking; 50 cc of the resulting fluid were transferred to a flat-bottomed dish and dried to constant weight at 100° C. The vacuum was not available, but a definite temperature on the water bath was maintained. The ether extract was determined by using anhydrous ether in a continuous extraction apparatus; extraction was continued 20 hours. The results obtained are given in the following table:

Analysis of the 18 powdered samples.

No.	Ash.	Insoluble.	Lime.	Water extract.	Starch.	Crude fiber.	Ether extract.	Aluminum + iron.	Remarks.
1.....	5.84	0.91	0.22	11.84	43.29	7.60	8.36	Trace...	African.
2.....	5.05	.43	.28	15.42	47.43	5.95	5.83	do.....	Jamaica.
3.....	5.66	.70	.24	14.34	42.07	7.56	8.31	do.....	Cochin.
4.....	3.64	.48	.23	12.61	60.30	4.89	4.32	Trace...	Jamaica.
5.....	5.14	.44	.16	13.37	43.83	6.89	7.30	do.....	African.
6.....	4.00	.40	.14	13.75	57.80	3.37	4.20	Trace...	Jamaica.
7.....	7.34	3.02	.15	11.01	39.15	5.14	4.90	do.....	Calcutta.
8.....	9.79	3.65	.25	14.31	32.12	7.02	8.11	do.....	Do.
9.....	5.83	.83	.34	11.98	51.23	6.91	7.52	do.....	Cochin.
10.....	6.39	.96	.32	15.97	54.45	4.50	6.57	do.....	Do.
11.....	5.28	1.43	.10	10.73	45.18	3.90	6.37	Trace...	African.
12.....	5.46	1.28	.11	12.50	51.39	7.16	7.49	do.....	Do.
13.....	5.31	.58	.88	11.42	51.39	6.40	4.57	Trace...	Japanese.
14.....	5.95	.54	1.56	13.57	55.08	3.80	6.26	do.....	Do.
15.....	3.41	.32	.14	12.22	55.44	3.72	3.25	Trace...	Jamaica.
16.....	3.92	.28	.14	14.20	57.78	2.72	4.62	do.....	Calcutta.
17.....	5.85	1.04	.06	10.57	34.12	7.90	8.89	do.....	Do.
18.....	7.18	2.06	.15	12.87	32.02	6.45	6.79	do.....	Do.
.....	6.0	3.0	1.00	42.00	8.00	Standard.
.....	10.0	4.00	42.00	8.00	Limed.

The Calcutta ginger and one Cochin ginger run high in ash. The others are all within the limits of the standard. The Calcutta ginger has an excess of insoluble ash. The lime content of one sample of Japanese ginger was high but considerably below the limit allowed for limed ginger. All samples were within the limits prescribed for crude fiber and starch, excepting the Calcuttas.

TINCTURES PREPARED FROM POWDERED SAMPLES.

Tinctures were next prepared from these samples in accordance with the Pharmacopœial instructions, and their characteristics observed after standing six months. The reason for making the observations at the end of six months

is that during this time the physical characteristics of many galenical preparations change materially. Tincture of ginger, however, is not apt to change very much. The points taken into consideration were sediment, color, specific gravity, residue, nonvolatile matter, and ash. The constants were determined in the usual manner. Color, however, was made a comparative determination by the use of a colorimeter, one of the samples of medium color being taken as a standard, and a length of column equal to 20 mm used. The numbers opposite the color in the table, therefore, represent the length of column of that sample which gave approximately the same color as the sample used as a standard.

Tinctures from powdered samples examined after standing for 6 months.

No.	Non-volatile.	Ash.	Sediment.	Color.	Specific gravity.
1..	Broken...				
2..	1.49	0.0055	None.....	Red-38.....	0.8128
3..	1.89	.0060	do.....	Red-27.....	.8147
4..					
5..	1.56	.0050	None.....	Dark-8.....	.8128
6..	1.13	.0312	do.....	Light-2.....	.8133
7..	1.04	.0030	do.....	Dark-18.....	.8116
8..					
9..	1.44	.0030	None.....	Medium-20.....	.8157
10..	1.19	.0380	do.....	Darker-14.....	.8130
11..	1.29	.0350	do.....	Deep red-16.....	.8133
12..	1.82	.0350	do.....	Deep red-16.....	.8147
13..	.99	.0100	do.....	Amber red-43.....	.8131
14..	1.75	.0100	Slight.....	Deep red-18.....	.8145
15..	.89	.0040	do.....	Very light-59.....	.8125
16..	1.40	.0060	None.....	Red brown-34.....	.8132
17..	.96	.0012	do.....	Red brown-29.....	.8134
18..	1.31	.0012	do.....	Red brown-17.....	.8134

These results corroborate the observations already made, namely, that the Calcutta and Japanese gingers are not suited for the manufacture of tincture of ginger. The degrees of fineness within the limits used in these investigations do not materially influence the amount of nonvolatile matter abstracted. These results clearly show that a good tincture of ginger should comply with the following requirements: Specific gravity at 25° C. not above 0.8270; alcohol, by volume, not less than 90 per cent; nonvolatile matter from 1.25 to 1.75 per cent. The figures clearly show that tincture of ginger made from Calcutta and Japanese gingers is of an inferior character. The tinctures made from Nos. 6 and 10 also contain a little less nonvolatile matter than the mean, but this is not sufficient to warrant more than a casual comment.

NOTE ON ASSAY OF NITROGLYCERIN TABLETS.

By A. G. MURRAY.

The methods which have been proposed for the determination of nitroglycerin are (1) the nitrometer method; (2) direct weighing of the ether extract; (3) saponification, and (4) the colorimetric method proposed by W. A. Scoville,¹ which is an adaptation of the well known method for nitrates in water analysis.

The nitrometer method is not well adapted to the estimation of nitroglycerin in medicinal tablets, on account of the small quantity present and the difficulty of introducing it quantitatively, and free from objectionable extraneous matter, into the nitrometer.

¹ Amer. J. Pharm., 1911, 83: 359.

Weighing the ether extract, where proper precautions to prevent loss are observed, yields entirely satisfactory results, provided, of course, the sample contains no other ether-soluble material.

Discussing the saponification method, Scoville calls attention to the discordant results recorded in the literature by Rice¹, Hay², and Beryl and Delpy³, and adds: "One has only to try the process, varying the conditions of heating, the time of standing, and the temperature, to become convinced that the results are of no value. Indeed, one is surprised to note how much variation in results is induced by slight variations in the process."

The differences in the results recorded by the authors mentioned are easily explained. Rice, who claimed that 3 molecules of potassium hydroxid are required to decompose 1 molecule of nitroglycerin, examined two commercial 10 per cent solutions, obtaining by his method 14.46, and 13.76 per cent respectively, and for six commercial 1 per cent samples he obtained results ranging from 1.18 to 1.81 per cent. He then diluted one of the 10 per cent samples so that, according to his analysis, it would contain 1 per cent. Duplicate analyses of this product by the same method of analysis gave 0.992 and 1.013 per cent, "which figures" the author concluded "prove the reliability of the method." There is no indication that the method was tried on a sample of known nitroglycerin content. Further consideration of this method is, therefore, unnecessary. The apparently high results obtained, if of any value, tend to prove that considerably more than 3 molecules of caustic potash are required to saponify 1 molecule of nitroglycerin.

Beryl and Delpy, who state that each molecule of nitroglycerin requires 6 molecules of potassium hydroxid, record only one experiment which they describe as follows: "Each 5 cc glycerin trinitrate was diluted with absolute ethyl alcohol to 100 cc, cooled to 4° and * * * slowly added to 100 cc alcoholic potash (10.5 grams potassium hydroxid in 100 cc 90 per cent alcohol). For each molecule of glycerin trinitrate there are about six molecules potassium hydroxid."

Considering the specific gravity of nitroglycerin to be 1.6 (Perkin, J. Chem. Soc., 1889, 55: 685), and assuming that the potassium hydroxid used was 100 per cent, the quantities used would represent 1 molecule nitroglycerin to 5.3 molecules potassium hydroxid, while if it is assumed that the alkali was 85 per cent, which is about the content of the grade usually found on the market for analytical purposes, the ratio of nitroglycerin to hydroxid is about 1 to 4.5. In view of what follows, it will be seen that there was not an excess of alkali, as stated by Berl and Delpy, and this is a possible explanation of the presence of glycerin dinitrate and unchanged trinitrate found in the reaction products.

The experiments of Hay were for the purpose of determining the nitrite produced by the saponification of nitroglycerin. The results of many experiments carried out under varying conditions show conclusively that the proportion of nitrite produced is sufficiently constant and independent of minor variations in the conditions to warrant the use of the method for quantitative estimations. Experiments are recorded by Hay in which the conditions varied from an excess of alkali to an excess of nitroglycerin, and from boiling the alcoholic solution on the steam bath for 30 minutes to saponifying in the cold for 2 minutes. The yield of nitrite varied within narrow limits. Hay showed that approximately 5 molecules of potassium hydroxid are necessary to saponify 1 molecule of nitroglycerin.

¹ Amer. Druggist, 1895, 27: 6.

² Trans. Royal Soc. Edinburgh, 1885, 32: 67.

³ Ber. d. chem. Ges., 1910, 43: 1421.

The method of estimation proposed by Hay depends on the determination of the nitrite produced by saponification, not on a titration with standard alcoholic potash and standard acid. Since small amounts of nitrous acid can be readily and accurately estimated, Hay's method is well adapted to the estimation of small quantities of nitroglycerin.

Scoville proposes to estimate nitroglycerin in tablets by evaporating the alcoholic extract, treating the residue with phenoldisulphonic acid, and determining the nitrate colorimetrically. The method is simple and gives excellent results. The substitution of ether for alcohol as a solvent improves the method. Ether can be rapidly evaporated in a vacuum. The temperature falls below zero, thus preventing any volatilization of the nitroglycerin with the ether. Ether does not dissolve any of the sugar usually present in the tablets, which is a decided advantage over alcohol, as the action of the sulphonic acid reagent on sugar is apt to produce a coloration which interferes with the accuracy of the test. Ethereal solutions do not require filtering, since the insoluble material settles very rapidly and the supernatant clear solution can be drawn off with a pipette. With alcohol the insoluble matter settles much more slowly. Sodium nitrate, which might be present as a decomposition product of nitroglycerin or as an accidental impurity, is insoluble in ether, but is soluble in alcohol and would be estimated as nitroglycerin.

There are, then, two methods suitable for the estimation of minute quantities of nitroglycerin. The weight of the ether extract and the determination of total nitrogen by the modified Gunning method frequently give additional useful information. The following outline is suggested as a convenient procedure in the analysis of nitroglycerin tablets:

Crush 25 tablets under 10 cc ether. A 25 cc cylindrical graduate makes a convenient container for the purpose. Decant the ether into a 50 cc graduated flask and wash the residue repeatedly with 5 cc portions of ether, finally making the solution up to the mark. It is immaterial if a little of the insoluble matter gets into the flask. Mix the solution thoroughly, allow any insoluble matter to settle, and carefully remove 20 cc of the clear solution with a pipette and place in a small tared dish or beaker. Place the beaker in a vacuum desiccator. With a good vacuum the evaporation will require only an hour or two. Weigh the residue. Treat with 2 cc of phenoldisulphonic acid reagent¹ and after 5 to 10 minutes dilute, wash into a 100 cc graduated flask, dilute to the mark, mix well, withdraw 10 cc representing 1 tablet, dilute nearly to 100 cc, neutralize with a few drops potassium hydroxid solution, and complete the volume to 100 cc. Compare the color with that produced by a standard nitrate solution similarly treated. Nitroglycerin is calculated by multiplying the nitrogen by 5.4.

To 5 cc of the ethereal solution add 5 cc of 0.5 per cent alcoholic potassium hydroxid, place on steam bath and allow most of the alcohol to boil off, add water and leave on the bath until the odor of alcohol is no longer perceptible. Dilute to 250 cc. Mix and place an aliquot representing 0.02 to 0.04 mg of nitroglycerin in a 100 cc graduated flask, add about 50 cc of water, 1 drop of concentrated hydrochloric acid, 2 cc of 1 per cent sulphanilic acid solution and 2 cc of 0.5 per cent naphthylamin hydrochlorid solution. Dilute to 100 cc and after 30 minutes compare the color with standard nitrite solutions similarly treated. Nitroglycerin is calculated by multiplying nitrite nitrogen found by 8.

The association adjourned.

¹ Details of the preparation of this reagent as given by Chamot, Pratt, and Redfield, J. Amer. Chem. Soc., 1911, 33: 382, may be followed.

OFFICERS AND REFEREES OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, 1911-12.

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Nitrogen:

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Sugar: M. N. Straughn, Washington, D. C.

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E. H. Jenkins, New Haven, Conn.

Presentation of the question of unification of terms to the International Congress of Applied Chemistry:

R. J. Davidson, Blacksburg, Va., chairman.
 C. G. Hopkins, Urbana, Ill.
 W. D. Bigelow, Washington, D. C.
 G. S. Fraps, College Station, Tex.
 B. W. Kilgore, Raleigh, N. C.
 H. J. Wheeler, Kingston, R. I.
 J. T. Willard, Manhattan, Kans.

Recommendation of referees and revision of methods.

[Figures in parentheses refer to year in which appointment expires.]

A. L. WINTON, chairman.

SUBCOMMITTEE A: W. W. Skinner (1916), B. B. Ross (1914), *J. P. Street* (1912), chairman, *Agricultural Experiment Station, New Haven, Conn.*

SUBCOMMITTEE B: H. E. Barnard (1916), *E. M. Chace* (1914), chairman, *Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C.*, J. M. Bartlett (1912).

SUBCOMMITTEE C: B. F. Trowbridge (1916); C. D. HOWARD (1914), *A. L. Winton* (1912), chairman, *U. S. Food and Drug Inspection Laboratory, Chicago, Ill.*

Testing of chemical reagents:

L. F. Kebler, Washington, D. C., chairman.
 A. L. Winton, Chicago, Ill.
 B. W. Kilgore, Raleigh, N. C.

Unification of methods of analysis of fats and oils.

L. M. Tolman, Washington, D. C., chairman.
 P. H. Walker, Washington, D. C.
 A. Lowenstein, Chicago, Ill.

CONSTITUTION OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

(1) This association shall be known as the Association of Official Agricultural Chemists of North America. The objects of the association shall be (1) to secure uniformity and accuracy in the methods, results, and modes of statement of analysis of fertilizers, soils, cattle food, dairy products, human foods, medicinal plants, drugs, and other materials connected with agricultural industry; (2) to afford opportunity for the discussion of matters of interest to agricultural chemists.

(2) Analytical chemists connected with the United States Department of Agriculture, or with any State, provincial, or national agricultural experiment station or agricultural college, or with any State, provincial, or national institution or body in North America charged with official control of the materials named in section 1, shall alone be eligible to membership; and one such representative for each of these institutions or boards, when properly accredited, shall be entitled to enter motions or vote in the association. Only such chemists as are connected with institutions exercising official fertilizer control shall vote on questions involving methods of analyzing fertilizers or involving definitions, nomenclature, laws, or regulations relating to fertilizers. Only such

chemists as are connected with institutions exercising official cattle-food control shall vote on questions involving methods of analyzing cattle foods or involving nomenclature, definitions, laws, or regulations relating to cattle foods. Only such chemists as are connected with institutions exercising official food or drug control shall vote on questions involving methods of analyzing food or drugs or involving nomenclature, definitions, laws, or regulations relating to food or drugs. All persons eligible to membership shall become members *ex officio* and shall be allowed the privileges of membership at any meeting of the association after presenting proper credentials. All members of the association who lose their right to such membership by retiring from positions indicated as requisite for membership shall be entitled to become honorary members and to have all privileges of membership save the right to hold office and vote. All analytical chemists and others interested in the objects of the association may attend its meetings and take part in its discussions, but shall not be entitled to enter motions or vote.

(3) The officers of the association shall consist of a president, a vice president, and a secretary, who shall also act as treasurer, and these officers, together with two other members to be elected by the association, shall constitute the executive committee. When any officer ceases to be a member by reason of withdrawing from a department or board whose members are eligible to membership, his office shall be considered vacant, and a successor may be appointed by the executive committee, to continue in office till the annual meeting next following.

(4) There shall be appointed by the executive committee, at the regular annual meeting, from among the members of the association, a referee and such associate referees for each of the subjects to be considered by the association as that committee may deem appropriate. [Construed by resolution passed in 1911 to mean the outgoing executive committee; standing rule adopted that the committee consult with each referee in the appointment of associates.]

It shall be the duty of these referees to prepare and distribute samples and standard reagents to members of the association and others desiring the same, to furnish blanks for tabulating analyses, and to present at the annual meeting the results of work done, discussion thereof, and recommendations of methods to be followed.

(5) The special duties of the officers of the association shall be further defined, when necessary, by the executive committee.

(6) The annual meeting of this association shall be held at such place as shall be decided by the association, and at such time as shall be decided by the executive committee, and announced at least three months before the time of meeting.

(7) No changes shall be made in the methods of analysis used in official inspection, except by unanimous consent, until an opportunity shall have been given all official chemists having charge of the particular inspection affected to test the proposed changes.

(8) Special meetings shall be called by the executive committee when in its judgment it shall be necessary, or on the written request of five members; and at any meeting, regular or special, seven enrolled members entitled to vote shall constitute a quorum for the transaction of business.

(9) The executive committee will confer with the official boards represented with reference to the payment of expenses connected with the meetings and publication of the proceedings of the association.

(10) All proposed alterations or amendments to this constitution shall be referred to a select committee of three at a regular meeting, and after report from such committee may be adopted by the approval of two-thirds of the members present entitled to vote.

BY-LAWS.

(1) Any amendment to these by-laws or addition thereto may be proposed at a meeting of the association and shall be published in the Proceedings. It may then be adopted by a majority vote of the association at the next meeting.

(2) These by-laws or any portion of them may be suspended without previous notice by a unanimous vote of those present at any meeting of the association.

(3) There shall be a committee of nine members which shall be designated as the committee on recommendations of referees. The president shall appoint three members of this committee to serve six years, such appointments to be made every other year as the terms expire. The chairman of the committee shall be appointed by the president and shall divide the nine members into three subcommittees (A, B, and C), and shall assign to each subcommittee the reports and subjects it shall consider.

(4) Each referee shall forward to the chairman of the committee on recommendations at least three weeks before the meeting of the association his recommendations and a sufficient abstract of his report to enable the committee to act intelligently on the recommendations.

As soon as possible after the annual meeting of the association each retiring referee shall transmit a copy of his report and recommendations, together with a statement of the action taken by the association upon the same, to the referee for the next year. [1911.]

(5) A method shall not be adopted as provisional or a provisional method amended until such method or amendment has been reported by the appropriate referee and published in the Proceedings of the association.

(6) A method shall not be adopted as official or an official method amended until such method or amendment has been recommended as official for at least two years by the appropriate referee.

(7) Each college, experiment station, bureau, board, or other institution entitled to representation in the association shall contribute annually \$2, and its representatives shall not be qualified to vote or hold office in the association unless such annual dues have been paid, but these shall not be cumulative.



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